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EXTRACTION OF VANADIUM AND NICKEL FROM ATHABASCA OIL SANDS FLY ASH

by

© PETER J. GRIFFIN

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF DOCTOR OF PHILOSOPHY

IN

METALLURGY

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EDMONTON, ALBERTA

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ABSTRACT

During the processing of bitumen from the Athabasca oil sands of northern Alberta, the fly ash produced is rich in many metals. The two plants currently in operation, Suncor and Syncrude, produce approximately 250 tonnes/year of ash containing 1-3% vanadium and 0.1-0.9% nickel. This thesis reviews the formation of ash and the extraction of metals from ash, attempts to characterize the ash and develops the optimum extraction procedures for recovering vanadium and nickel.

Vanadium extraction of 90% can be obtained by roasting Suncor ash with sodium chloride and leaching with hot water. A similar nickel extraction can be obtained by roasting Suncor ash with sulphur and leaching with sulphuric acid. Only vanadium can be extracted from Syncrude ash after carbon removal. The vanadium extraction solution is suitable for direct treatment to form a vanadium pentoxide product, but the nickel extraction solution may require further treatment prior to nickel recovery.

Suncor ash consists of distinct coke grains and aluminosilicate spheres containing the metallic components. The extraction chemistry indicates that the spheres may contain an iron vanadium oxide and a nickel laterite.

PREFACE

If many faultes in this book you fynde,
    Yet think not the correctors blynde;
If Argos heere hymselfe had beene
    He should perchance not all have seene.

Richard Shacklock, 1565

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I. INTRODUCTION AND LITERATURE REVIEW

Over 50 million tonnes of fly ash are currently produced annually in North America from coal, coke and oil combustion processes. Although the ash is mainly a silicate material, it may also contain significant quantities of many metals.

At present only 10-15% of the available fly ash is utilized other than in land fills. This use in cement, concrete, soil stabilization, road beds, ceramics, mineral wool, fertilizers and brick manufacture is reviewed by Capp and Spencer[1] and is a growing field.

Recent legislation[2] in the United States has stated that certain leachable materials must be removed from ash dumps and this may stimulate an examination of the possible recovery of metals from fly ash. Previous studies have examined the possibility of extracting iron, aluminium, titanium, nickel and several other elements but only vanadium, germanium and gallium are currently produced from ash.

This thesis will concentrate on the extraction of vanadium and nickel from ash derived from the Athabasca oil sands, primarily from the Suncor operation.

Rosenbaum[3] has reviewed the history, occurrence, processing and use of vanadium. Updating this review, the current annual western world vanadium consumption is 37 million kilograms of V_2O_5, far below the production capacity of 50 million kilograms. Other plants are under construction to increase production capacity by 10%, including a 1.8 8million kilograms per year plant in Oklahoma utilizing boiler ash.

However, over 90% of the world's vanadium reserves are either in the countries of southern Africa or in the Soviet Union. Recently, it has been reported[4] that the Soviet Union has begun to import vanadium, although still a net exporter, and is no longer contracting to export nickel. Thus, it is possible that the West will require secure sources of these and other strategic metals to avoid possible supply problems in the future.

It has been estimated[5] that up to 1025 tonnes/year of vanadium will be potentially recoverable from the Athabasca oil sands area; this is equivalent to 5% of the world consumption and 700% of the Canadian consumption. The nickel content of the ash is less than that of vanadium and is only a very small fraction of the current annual Canadian production of 272,000 tonnes. The current annual vanadium and nickel content of the fly ash production from the oil sands is approximately 540 tonnes and 190 tonnes, respectively.

The following literature review will initially discuss the formation, structure and composition of fly ash, followed by a survey of the suggested extraction techniques for the recovery of metals from ash. Finally, the formation and chemical composition of the Athabasca fly ash will be reviewed and the few existing studies of vanadium and nickel in the coke and ash examined.

A. ASH FORMATION & STRUCTURE

Particle Formation

Coal combustion is a major source of particulate emissions which may include soot, char, fly ash and acid droplets. The physical and chemical structure of the emissions depends not only on the coal composition, but also on the firing scheme and the time-temperature history of the ash. The effect on the environment of the fine particle emissions has led to much of the recent work on ash formation and composition.

Initially, during coal or coke combustion, any remaining volatile hydrocarbons are removed along with extremely volatile elements such as mercury. The burning of the hydrocarbons may also vaporize any metals associated with the organic material such as vanadium and nickel in porphyrins. Flagan and Friedlander[6] have reviewed the formation of ash and they present the following series of events:

<500°K - dehydration; changes in mineral form

<800°K - FeS oxidized

<1100°K - carbonates and sulphates decompose

>1350°K - alkali salts volatilized

>1900°K - SiO_2 volatilizes by reduction to SiO.

Ramsden[7] has suggested that the mineral inclusions in the coal melt as the combustion front approaches. They then agglomerate, as the remaining carbon is oxidized, to form spherical particles. The molten ash has a high surface tension and does not wet the coal. Flagan and Friedlander have also presented a mathematical model of this system which they report as being in good agreement with the data of McCain et al.[8] for particles above 1 μm in diameter. However, their model is very sensitive to the value given a constant in the relationship and they make a possibly erroneous assumption. They assume that each coal particle produces a constant number of ash particles independent of coal particle size.

The presence of hollow fly ash spheres, cenospheres, has been explained[6] as being caused by the evolution of gas inside the ash spheres when they are in a slighty fluid state. Pleurospheres, cenospheres with internally trapped particles, are suggested[7] to occur by initial gas evolution to form a cenosphere. As the pressure drops below atmospheric outside the combustion zone, the molten interior "buds off" to form small interior spheres.

The mathematical model used by Flagan and Friedlander[6] does not account for particles smaller than the smallest mineral inclusion. The generally accepted explanation for the fine material, first suggested by Ramsden,[7] is that rapid internal gas evolution may cause the spheres to shatter into fine particles. Other possibilities are condensation of volatiles on soot particles or homogeneous nucleation but these have been disproved by chemical analyses.[10]

Volatile Enrichment

Collection of fly ash from many different sources and subsequent sizing and chemical analysis has shown that the concentration of some elements has a dependence on the particle size of the ash. The generally accepted explanation is that volatile elements or oxides present in a gaseous form during combustion, condense onto fly ash particles as the temperature drops.

If we assume that an element X has partially condensed, in some form, on the surface of a sphere of diameter D, then

$$O = M + S$$

where M = mass of element X in the sphere interior

S = mass of element X on the sphere surface

O = mass of element X in the total sphere.

The total concentration of X is then given by:

$$C_a = C_m + \frac{C_s A}{\rho V}$$

where C_m = sphere interior concentration of X (mass per unit mass)

C_a = overall concentration of X (mass per unit mass)

C_s = surface concentration of X (mass per unit area)

ρ = particle density

V = particle volume

A = particle surface area.

By assuming sphericity, the average concentration of X, C_a, is given by:

$$C_a = C_m + \frac{6\ C_s}{\rho\ D}$$

Simply, this vaporization-condensation model suggests a relationship of $C_a \alpha D^{-1}$.

The thickness, T, of the deposition layer can then be estimated from the expression,

$$T = \frac{C_s}{\rho'}$$

where ρ' is the density of the deposition layer. Existence of a deposition layer has been confirmed for Fe, Cr, Ni and S by Hulett et al.[11] using scanning electron microscope analysis and by Natusch et al.[1] using an ion microprobe, Auger microprobe spectroscopy and electron microprobe spectroscopy for Cr, K, Na, P, Pb, S and Zn.

The particle size-concentration trends have been studied by many authors[1-21] and their evaluated relationships are presented in Table 1 along with the number of reported occurrences of each relationship. It should be noted that several elements obey different relationships in various ashes, due to varying production schemes.

The deficiency of some elements in the fine fraction of the fly ash is due to the reduced proportions of matrix material to surface elements in these fractions, i.e., the deposition layer is a larger proportion of the total material in the finer sizes.

As some of the enriched elements have compounds with low melting points, they are believed to exist in a gaseous form in the deposition zone. Kaakinen et al.[15] found that the enrichment of Cu, Sb, Zn, As, Mo and Pb over the other elements was in agreement with the higher volatility of their oxides. Shroeder[22] suggests that the volatility of nickel and chromium may be due to the presence of carbonyl and sulphide forms respectively.

Fisher et al.[17] stated that uranium and chromium are associated with organic material. They are released on burning and condense onto the fly ash particles. Another study[9] reported that the preferred condensing element depends on the particle matrix. This was shown as antimony condensed preferentially on magnetic particles; arsenic preferred high density ones; and barium and manganese preferred high density non-magnetic particles. Davison et al.[18] have calculated the deposition layer thicknesses shown in Table 2.

Superficially, the vaporization-condensation model is in excellent agreement with the observed concentration variation in many ashes. However, the model assumes that the layer is infinitessimally thin and no studies had been carried out on particles in which the layer becomes a large proportion of the particle.

Element	C_s (ng/cm^2)	C_m (mg/g)	T (Å)
As	9	0.6	0.3
Cd	2	0.02	0.7
Cr	300	0.3	9
Ni	100	0.1	4
Pb	40	1	1
Sb	3	0.02	0.1
Se	4	0.0007	0.1
Tl	3	0.04	0.1
Zn	600	6	20

Table 2. Deposition layer thicknesses

Smith et al.[10] extended the previous model of an infinitesimally thin deposition layer to the situation in which the particle diameter increases due to the layer. They presented concentration equations for two cases; these were T being independent of particle size and T being inversely proportional to particle size. The second case assumes that the time particles spend in the deposition zone is inversely proportional to the particle size.

The study also reported that many element (As, Pb, Mo, Hg, Se, Sb, Sn, V, Cu, Ni, Zn, Ga and Cr) concentrations were independent of particle size below about 0.8 µm, i.e., material supposedly formed by the shattering of cenospheres.

Smith et al. considered the various mechanisms for the formation and constant element concentration of the submicron fly ash, and their accepted explanation involves:

> "Formation by "bursting" of larger particles during rapid gas release and subsequent coagulation of much smaller fragments. Condensation of volatilized material may occur during and after formation....(The process) would lead to the type of (particle) uniformity...and surface enrichment observed."

This relationship is in close agreement with actual elemental variations over the size range examined (0.2-200 µm). Additionally, they suggest that their value of X may be dependent on the combustion temperature and that further studies may determine the mode and quantities of particles formed under various combustion conditions.

Composition and Structure

Elemental analyses of numerous coal and coke fly ashes have been made primarily for environmental reasons and Tables 3 and 4 show the reported concentration ranges.[9-26]

The components of fly ash are generally reported as being "glassy" but five X-ray diffraction studies[19,22,23,27] have variously identified quartz, mullite, hematite, magnesium orthovanadate, magnetite, calcite, pyrite and an iron silicate glass.

A recent study* identified three components in fly ash: glass, mullite-quartz and magnetic spinel. The trace elements are distributed in various proportions in the three phases; vanadium is equally present in each phase, nickel is concentrated in the magnetic spinel phase.

---

*Hulett, L.D., Weinberger, A.J., Northcutt, K.J. and Ferguson, M., "Chemical Species in Fly Ash from Coal-Burning Power Plants," Science, 210, pp 1356-8, 1980.

Element	Percentage
Al	7-15
Ba	0.1-12
Ca	0.2-15
Ce	0.1-8
Fe	1.5-15
K	0.1-2.6
Mg	0.7-6
Mn	0.1-2
Na	0.1-2
Pb	0.006-5
Si	22-30
Sr	0.5-2.3
Ti	0.3-20
V	0.05-2.3
Zn	0.01-2
Zr	0.02-1.4

Table 3. Major elemental components of fly ash

Element	ppm	Element	ppm
Ag	12	Nb	70-180
As	3-350	Nd	83
Be	1-10	Pr	20
Cd	0.01-100	Pd	5
Co	7-100	Ru	6
Cr	10-1000	Rh	5
Cu	10-1000	Rb	40-140
Cs	4-5	Sm	9-25
Dy	8-20	Sb	0.01-100
Eu	2-6	Sn	2-100
Ge	33	Sc	25-50
Ga	40-165	Se	1-75
Hg	5	Te	13
Hf	30	Tb	1-4
In	14	Ta	3-10
Li	0.1-300	Th	35
La	70-105	Y	50-115
Lu	2.5	Yb	4-11
Mo	10-1000	U	15
Ni	30-1000		

Table 4. Minor elemental components of fly ash

B. RECOVERY OF VANADIUM FROM ASH

Extraction of vanadium has been considered many times from ashes with various sources. In most cases, a final extraction route has been suggested without detailing:

1. the other extraction routes examined,
2. the characteristics of the ash, and
3. the chemical explanation of the extraction.

This section of the review will discuss two well-documented industrial extraction processes for the recovery of vanadium from ash. It will also summarize the various patents and publications dealing with the extraction of vanadium.

Petrofina

The Petrofina refinery in Quebec used Venezuelan crude oil averaging 130 ppm vanadium. Until 1961 the fluid coke produced was sold for fuel and electrode manufacture. A coke fired steam boiler was then installed to use 50% of the 100 tonnes/day coke production. The addition of an electrostatic precipitator in 1964 produced ash which contained approximately 20% vanadium pentoxide.[28]

In 1962 Petrofina contracted with the Mines Branch in Ottawa to investigate a possible process for the extraction of vanadium from the boiler fly ash. The results were published in 1965.[29]

Three direct leaching mediums were considered; they were soda ash, nitric acid and sulphuric acid. The maximum extractions of vanadium obtained with these reagents were

81.4%, 96.6% and 94.1%, respectively. The final decision to recommend sulphuric acid leaching to Petrofina was made due to the significantly lower acid concentration required to obtain over 90% extraction. The final process suggested by the Mines Branch consisted of sulphuric acid leaching, oxidation of the vanadium solution and precipitation by ammonia, followed by calcining to vanadium pentoxide.

This recommendation was accepted by Petrofina and a plant was constructed in 1964 to produce 545 kg V_2O_5/day. The process flow sheet is shown in Fig. 1.[30] In 1965 the process was producing 3% of the world's vanadium supply at a cost of $2.2/kg V_2O_5 compared to a market price of $2.75. This process continued operation until the mid-1970's when the vanadium-rich crude oil was no longer refined by Petrofina.

LILCO

LILCO (Long Island Lighting Company)[27, 31] first sold high grade vanadium ash from the combustion of Venezuelan fuel oil in 1964. By 1973 the company was producing 0.7% of the American power requirement and 5.5% of the American vanadium requirement.

The oil contains approximately 0.1 kg V_2O_5 per barrel. In 1976, 13.7 million barrels produced 1.2 million kilograms of vanadium pentoxide. Approximately 30% of the ash is collected as high grade furnace bottom ash containing 35-40% V_2O_5 present as magnesium orthovanadate (due to the addition

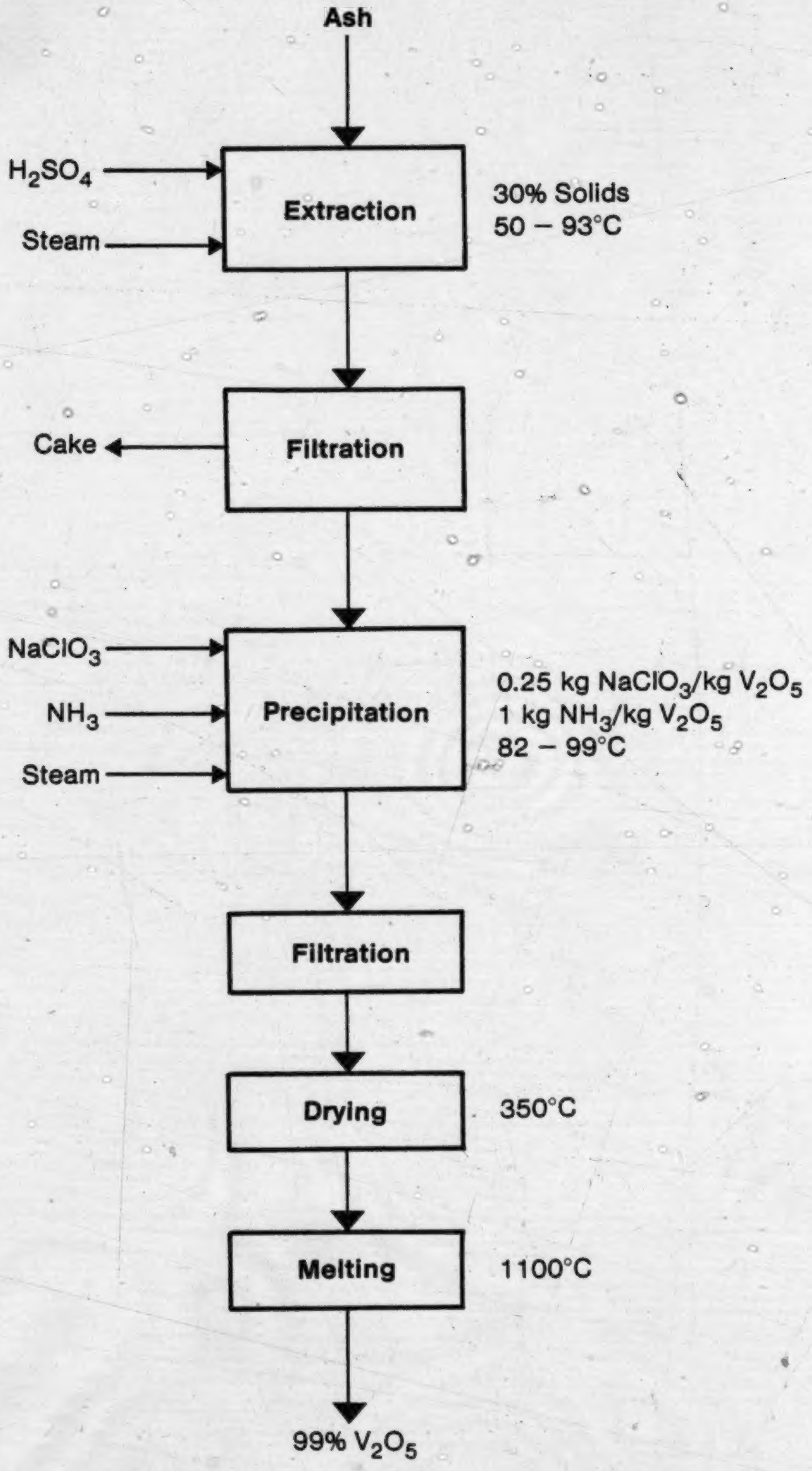

Ash
H_2SO_4
Steam
Extraction
30% Solids
50 – 93°C
Cake
Filtration
$NaClO_3$
NH_3
Steam
Precipitation
0.25 kg $NaClO_3$/kg V_2O_5
1 kg NH_3/kg V_2O_5
82 – 99°C
Filtration
Drying
350°C
Melting
1100°C
99% V_2O_5

Figure 1. Petrofina vanadium extraction process

of magnesium to the oil).

The high grade ash is sold to various vanadium producers for treatment with ferrophosphorous slags and imported iron ore slags. Prior to 1971, the low grade ash, collected during gas cleaning, was stored in a water pond. From 1971 to 1976, the ash was dredged from the pond and sold for vanadium recovery.

This storage technique had the disadvantages of vanadium dissolution, ground water contamination and sand contamination of the dredged ash. LILCO then developed a filtration-clarification system with pH adjustment to prevent vanadium dissolution. A plant is presently being constructed based on this process with additional ash washing to remove sulphates and roasting to lower carbon content.

Patents

Numerous patents and brief studies of the recovery of vanadium from various ashes have been published, particularly in Japan. Virtually all common extractive techniques and some novel ones have been attempted, but rarely has more than one process or ash been studied simultaneously.

a. Direct Leaching

Direct leaching of fly ash for vanadium recovery has been reported as being successful for a wide range of systems.

The simplest leaching system with hot water has been studied often.[32-38] One study[34] has reported the crystallization of a nickel salt on cooling and the production of V_2O_5 by oxidation of the solution with hydrogen peroxide. Another[35] reports the crystallization of sodium sulphate and oxidative precipitation of V_2O_5 by potassium perchlorate. Other processes have examined leaching under sulphur dioxide atmosphere,[36] precipitation with ammonia[37] and oxidation with sodium perchlorate.[38]

The major studies on acid leaching have involved sulphuric acid.[39-47] Precipitation of vanadium pentoxide has been achieved by ammonia,[39, 40] pH adjustment[41] and, oxidation and hydrolysis.[42, 43] Three reports have presented unusual purification schemes after acid leaching:

a. pH adjustment to 1.5-2.0 and vanadium precipitation by iron,[44]
b. sulphur dioxide contact to reduce Fe^{3+}, alkyl phosphate solvent extraction of vanadium and NiS formation by alkali sulphide addition to the barren solution,[45]
c. a three stage solvent extraction process using a tertiary fatty acid and di-2,5-ethyl-hexylphosphoric acid in kerosene, extracting iron, vanadium and nickel.[46]

Other acid extractions have involved recovery by ion exchange after oxidation[48] and precipitation by ammonia after hydrochloric acid leaching.[49]

Leaching with basic solutions has been suggested using sodium carbonate[50] and sodium hydroxide.[50] [51] Other studies have reported leaching with ammonia[52-54] and sodium oxide.[55] These basic solutions can be purified by calcium hydroxide additions which precipitate dissolved silicon and aluminium.[51] [55]

An unusual scheme[56] suggests leaching successively with three solutions; 10% H_2SO_4, 10% $CaCO_3$ and 10% H_2SO_4. The vanadium is apparently extracted only in the last stage. Uesaka and Ueno[57] reported leaching with 5% hydrogen peroxide and precipitation by hydrolysis.

b. Pre-leach roasting

Pre-leach roasting with various additives has been suggested as the best extraction route for many ashes. These additives have included:

sodium carbonate/sodium nitrate,[35] [58]
sodium hydroxide,[59-62]
potassium hydroxide/sodium hydroxide,[63]
sodium carbonate,[64] [65]
sodium hydroxide/potassium nitrate,[66]
sodium chloride,[67-69]
potassium hydroxide[70] [71]
aluminium oxide/sodium chloride.[72]

The majority of these roasts occur at 500°-900°C and the resultant material is leached with water. The solution can then be treated for vanadium recovery by pH adjustment, oxidation followed by hydrolysis, or precipitation with ammonia.

Lukomskaya and Bulankina[67] leached their salt roasted ash with an 8% sodium carbonate solution and precipitated iron vanadate. Another study[64] leached with quebracho and precipitated vanadium with gelatin, after initial roasting with sodium carbonate.

Direct roasting in air has been studied followed by acid leaching and pH/$NaClO_4$ precipitation[72] or hydrogen precipitation.[73] Sulphidizing roasts have also been reported as having been successful.[32]

A rather extensive patent[74] issued to Vojkovic in 1973 includes different types of treatment for vanadium containing materials. It also states results for identical leaching conditions that vary by a factor of two. The recommended process for ash involves roasting in argon with 25% sodium carbonate at 625°C, then roasting in air at 900°C, followed by water leaching, achieving 88% vanadium extraction.

c. Miscellaneous

Two reports[32] [64] suggested the use of direct chlorination and leaching but no results were presented. One of many Japanese studies[68] roasted with sodium chloride at 500°-700°C to directly volatilize $VOCl_3$.

A Japanese patent[75] states that the vanadium content of a Kuwaiti oil can be reduced from 7 ppm to 0.3 ppm and nickel from 26 ppm to <0.05 ppm by contacting it with a nickel ore at 500°C, thus preventing the formation of a metal-rich ash.

Sato and Yano[76] [77] have reported the direct smelting of the ash, after carbon and sulphate removal, to produce a FeVNi alloy or a Fe-VC-Ni cermet.

The extraction of vanadium from the residues of oil shale processing has also been considered. The suggested approaches are either carbonate roasting and water leaching,[78-81] or salt roasting and sulphuric acid leaching.[82]

C. RECOVERY OF NICKEL FROM ASH

Extraction of nickel from combustion residues has been considered only as related to vanadium extraction. In many of the nickel recovery processes, nickel is essentially removed from a vanadium-containing solution as a purification step:

a. after an acid leach, iron and nickel are removed from the vanadium containing solution by a cation exchange resin,[38] [48]

b. after a hot water leach, a nickel ammonium salt crystallizes from the vanadium solution on cooling,[34]

c. after a hot water leach, nickel is precipitated from the solution by the addition of 150 g/l ammonium sulphate,[42] and

d. another study reports that after sulphuric acid leaching, nickel can be precipitated on cooling if ammonium sulphate is added.[43]

Other experimental studies suggest recovering nickel from the residue ash or waste solution after vanadium recovery:

a. three studies suggest precipitating NiS from the waste solution, after vanadium recovery, by the addition of alkali sulphides,[45] [49] [72]

b. after successful leaching of vanadium by hydrogen peroxide, Uesaka and Ueno[57] state that hot water leaching will dissolve nickel,

c. Amaha[53] extracted nickel by hot water leaching of the residue from ammonium sulphate leaching of vanadium, and

d. a patented Japanese process[46] extracted iron, vanadium and nickel successively from the leached solution by solvent extraction with a tertiary fatty acid, di-2,5-ethylhexylphosphoric acid and a tertiary fatty acid, respectively.

The remaining leaching processes either do not comment on the recovery of nickel from the solution[40] [44] or else co-precipitate vanadium and nickel by ammonia.[35] [39]

The process of Asano et al.[48] which volatilizes $VOCl_3$ by roasting the ash with sodium chloride is reported as leaving the nickel as nickel chloride.

The ash used for vanadium recovery at the Petrofina refinery contains approximately 1% nickel. Leaching of the ash dissolves 75-80% of the nickel which remains in the final waste solution at a concentration of 1.5 g/l.

D. EXTRACTION OF OTHER METALS FROM ASH

The large quantity of ash produced in North America will increase due to the decreasing use of oil and the increasing use of high ash content western U.S. coals. Table 5 shows the estimated quantities of various metals in North American ashes and the western world, U.S. and Canadian production of those metals. The metals for which ash contains a major fraction of North American production include: aluminium, cobalt, gallium, germanium, selenium and vanadium.

Aluminium, Iron and Titanium

The possibility of recovering alumina or aluminium from fly ash has been examined several times, initially by Pedersen in 1927.[83] The normal extraction route involves caustic soda dissolution and alumina trihydrate or sodium aluminate precipitation.[84-95] Other techniques examined include hydrofluoric acid leaching,[96] roasting with ammonium sulphate/ammonium fluoride at 400°C to form aluminium sulphate[97] and the possible recovery of aluminium chloride by direct chlorination.[98] Two Dutch patents by Dorren and Freling[99] [100] state that the addition of 2.5 wt % of a Group II hydroxide to coal before combustion produces an ash in which 80% of the aluminium is soluble in concentrated hydrochloric acid.

Studies on several different ashes containing 2-15% iron have reported[95] [101-107] that a magnetic separation of

Metal	Ash content	US production	Canadian production	Western World production
Al	5,260,000	4,557,000	844,500	11,980,000
Be	250	c190	-	260
Cd	500	1,750	3,450	13,400
Co	1,000	500	3,000	28,000
Cu	2,270	1,980,000	425,000	7,030,000
Ga	1,500	c7	1	1,000
Ge	1,500	13	7	90
Mo	1,000	63,800	10,200	87,000
Ni	1,500	12,800	272,000	567,000
Pb	2,720	1,184,000	184,200	3,878,000
Sb	50	680	1,550	51,000
Se	270	270	260	1,170
Sn	140	c57,000	-	171,800
U_3O_8	1,150	c17,800	6,830	49,550
V	5,000	c6,030	c140	22,660
Zn	5,000	487,500	1,160,000	2,527,000

c: consumption

Table 5. Comparison of metals production and ash content(tonnes)

the ash produces an iron rich fraction suitable for processing as an iron ore. Two of these studies[106] [107] state that the nonmagnetic ash fraction contains up to 30% alumina and may be suitable for aluminium production.

The nonmagnetic fraction of one power plant fly ash[108] containing 8% titanium dioxide was directly chlorinated at 900°C to recover over 60% of the metal as titanium tetrachloride. However, the high iron content (10% Fe_2O_3) consumed 75% of the chlorine to form iron chloride, thus making the process uneconomic.

Germanium and Gallium

Morgan[109] first commented on the high germanium and gallium content of Northumberland coal ash in 1935. This resulted in a process developed by Morgan and Davies[110] in 1937. Their recommended process involved leaching of the ash with hydrochloric acid and distillation of germanium tetrachloride (b.p. 84°C) from the solution. Contamination by arsenic trichloride can be removed in a fractionating column. This process has also been recommended by Stovik and Tyroler,[111] and Gitter et al.[112] for germanium recovery from flue, coal and pyrite dust.

The majority of the other processes suggested for germanium recovery from fly ash and similar materials utilize the high volatility of $GeCl_4$:

a. direct chlorination of the ash at high temperatures to produce $GeCl_4$[113-115]

b. dissolution of germanium with alkali sulphide or sodium hydroxide solution, acidification with HCl followed by distillation of $GeCl_4$,[112, 116-118]

c. direct hydrochlorination at 700°C to form $GeCl_4$.[119]

d. roasting at 1350°C to form an iron-germanium alloy followed by direct chlorination to $GeCl_4$.[120]

Other reports have suggested leaching germanium with sulphuric acid,[121] hydrochloric acid,[122] or dilute acid leaching of salt roasted ash followed by precipitation with chestnut tanning and roasting to form germanium dioxide.[123]

A pyrometallurgical process for the recovery of germanium and gallium was developed in the late nineteen-forties by the General Electricity Council and Johnson Matthey Company Limited in the United Kingdom.[124, 125] The process involves smelting flue dust with soda and lime as fluxes for silica and alumina. The addition of copper oxide enables collection of 90-95% germanium and 50-60% gallium in a copper-iron alloy.

The alloy is then treated with dilute ferric chloride solution and chlorine gas followed by distillation of the solution. The distillate is purified and hydrolyzed to form germanium dioxide; the residue is purified and electrolyzed to form gallium. Since 1950, the entire U.K. source of germanium has been from coal ash flue dust, at a rate of approximately 500 kg annually.

It has been recently suggested[126] that gallium may be extracted from coal fly ash by the use of induction plasma.

Beryllium, Copper, Lead and Molybdenum

Recovery of beryllium from ash containing 800 g/tonne, produced from a Russian lignite coal, has been suggested by Vratislav.[127] An 80% recovery was obtained by treating the ash with concentrated sulphuric acid and extracting the beryllium from the solution with di-2,5-ethylhexylphosphoric acid in kerosene.

Vetejska[128] has reported that sulphuric acid will leach copper from fly ash but combustion above 850°C will form insoluble copper ferrite.

Another Russian study of the possible utilization of coal ashes[129] used an ash containing 22 kg Pb/tonne and which can be pyrometallurgically beneficiated to 120 kg/tonne.

Fester and Martinuzzi[44] have reported the extraction of molybdenum, in addition to vanadium and nickel, from asphalt ashes by sulphuric acid leaching. Mirzakarimov[130] has examined an ash containing 0.16-0.24% molybdenum and obtained some extraction by leaching with 0.15 M sodium carbonate solution.

Uranium

Presently, the economic grade for uranium mining is approximately 0.08% U_3O_8. An examination of the metal content of various U.S. ashes[22] has shown that the ash from some western lignites contains up to 0.5% U_3O_8. Additionally, some lignites and carbonaceous shales in the

Dakotas contain an average of 0.18% U_3O_8. In Yugoslavia, bituminous shale containing 136 g U/tonne and ashes containing 0.1-0.2% U_3O_8 have been identified.[131]

The only leaching study[128] suggests that acid leaching efficiency is independent of combustion temperature and that alkali leaching efficiency decreases with increasing combustion temperature. However, no extraction efficiencies were reported.

Multi-Element Extraction Studies

Three recent reports[79] [132] [133] have commented on the extraction of several elements and compounds from ash by various treatment schemes, rather than concentrating on the extraction of a specific element.

Gony and Cossais[132] treated ash produced from the incineration of refuse in a variety of ways and their results can be summarized as:

a. tin, lead and zinc were concentrated in the fine ash (<20 μm),
b. concentrated acid solutions extracted 50% of the tin and 70-90% of the lead, zinc, copper and iron from the crude ash,
c. acid solutions extracted over 60% of the copper from the air roasted ash,
d. 12 N hydrochloric acid leached 80-95% of the tin, lead, copper and iron from ash roasted in a reducing atmosphere.

Staff at the Oak Ridge National Laboratory (ORNL) have carried out a detailed engineering analysis and cost comparison for the utilization of a typical fly ash (23% Si, 15% Al, 7% Fe), at a rate of 1 million tons per year, by various processes aimed at producing alumina and other products.[133] The processes examined were also studied experimentally by ORNL[79] and are shown below.

Salt-Soda Sinter

Process: magnetic ash removal; 1000°C sinter with sodium chloride/sodium carbonate; leach with dilute H_2SO_4; solvent extraction (SX) with Primene JM-T.

Products: alumina from leach solution; silica gel from leach residue; manganese and titanium from SX.

Costs: Raw materials \$85/ton alumina.
Capital cost $\$66 \times 10^6$.
Utilities \$30/ton alumina.

Profit: \$30/ton alumina.

Calsinter

Process: magnetic ash removal; 1300°C sinter with calcium carbonate/calcium sulphate; leach with 3 N H_2SO_4; SX with Primene JM-T.

Products: alumina; manganese and titanium; cement from leach residue.

Costs: Raw materials \$56/ton alumina.
Capital cost $\$72 \times 10^6$.
Utilities \$65/ton alumina.

Profit: \$30/ton alumina.

Direct Acid

Process: leach with 8 M HNO_3; SX with di-2,5-ethylhexylphosphoric acid.

Products: alumina; manganese and titanium.

Costs: Raw materials $55/ton alumina.
Capital cost $58 x 10^6.
Utilities $40/ton alumina.

Profit: $34/ton alumina.

Lime-Soda Sinter

Process: magnetic ash removal; 1250°C sinter with calcium carbonate/sodium carbonate; leach with dilute sodium carbonate solution.

Products: alumina; cement.

Costs: Raw materials $120/ton alumina.
Capital cost $62 x 10^6.
Utilities $57/ton alumina.

Loss: $60/ton alumina.

Byproduct recovery was also suggested as being possible from the leach solutions, by solvent extraction or ion exchange, for the following elements: iron, uranium, thorium, vanadium, bismuth, gallium, molybdenum and antimony.

E. ALBERTA OIL SANDS

The first white man to discover the northern Alberta oil sands was the fur trader Peter Pond in 1778. Development of commercial oil sands technology commenced after K. A. Clark's laboratory studies of bitumen extraction from 1900 to 1950.

It is now estimated[134] that the northern Alberta oil sand deposits contain 900×10^9 bbl (143×10^9 m^3) of bitumen from which only 25×10^9 bbl (4×10^9 m^3) are estimated to be recoverable by surface mining and processing. The distribution of bitumen in the major fields in Alberta is shown in Table 6. At present, two commercial plants utilize surface mining of the Athabasca deposit. Other plants are planned and pilot plants are in operation on the Athabasca, Peace River, Wabasca and Cold Lake deposits using in situ recovery techniques.

Suncor

The first major commercial oil sands operation commenced in 1967, operated by Suncor Inc., formerly Great Canadian Oil Sands (GCOS). Initially designed to produce 7,200 m^3/day of synthetic crude oil it will be soon capable of producing 9,200 m^3/day. A detailed examination of the mining and extraction operation can be found elsewhere,[135] but Fig. 2 presents a brief outline of the extraction process and products.

Location	Overburden (m)	Area (10^3 ha)	Bitumen (10^9 bbl)
Athabasca	0-46	198	74
	46-610	2129	552
Cold Lake	305-610	1279	164
Peace River	305-762	478	50
Wabasca	76-762	714	54

Table 6. Major oil sands fields

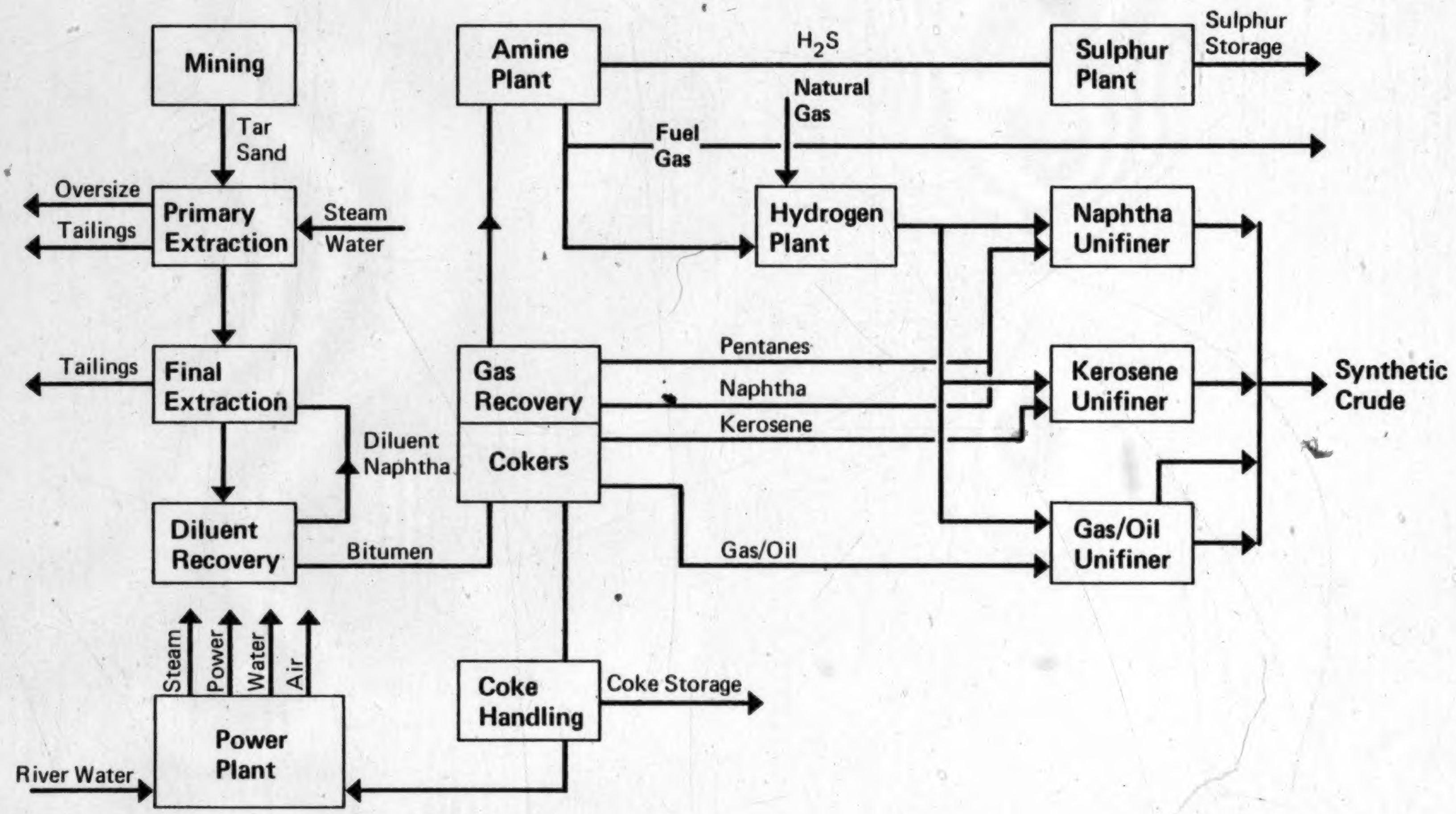

Mining
Tar Sand
Oversize
Tailings
Primary Extraction
Steam
Water
Tailings
Final Extraction
Diluent Naphtha
Diluent Recovery
Bitumen
Steam
Power
Water
Air
Power Plant
River Water
Amine Plant
H_2S
Natural Gas
Fuel Gas
Sulphur Plant
Sulphur Storage
Hydrogen Plant
Gas Recovery
Cokers
Pentanes
Naphtha
Kerosene
Gas/Oil
Naphtha Unifiner
Kerosene Unifiner
Gas/Oil Unifiner
Synthetic Crude
Coke Handling
Coke Storage

Figure 2. Oil sands treatment process[135]

The Suncor operation consumes approximately 150,000 tonnes/day of oil sand producing 13,500 tonnes/day of bitumen as feed for the cokers. The typical composition of the bitumen is shown in Table 7. Vanadium and nickel are partially present in the bitumen as organometallic porphyrins.

The bitumen is fed to a fractionator, mixed with recycle material and is sent to a coke heater. Partial volatilization occurs and the vapor and solid are sent to the coke drums which are held at 480°-500°C and at pressures of 20-60 psig (138-414 kPa) for 22 hours. Approximately 22% of the bitumen is converted to coke and removed from the coke drum by hydraulic cutting. The vapour re-enters the fractionator and separates as gas, oils and recycle material.

At present, approximately 2,450 tonnes/day of coke is produced, with the bulk (2,000 tonnes/day) being sent to Foster Wheeler boilers for the production of steam by firing at 900°C. The remaining coke is normally stockpiled, but recently(36) 20,000 tonnes was sold for the production of cement to a Japanese company. Table 8 shows the typical composition of the Suncor coke.

The firing of the coke produces little bottom ash and the metal content of the coke is collected in the various ash fractions. Prior to 1980, the fly ash was collected from the boiler effluent by cyclotrells; now the cyclotrells have been replaced by electrostatic precipitators (ESP).

Component	Bitumen content
V	150-200 ppm
Ti	110 ppm
Ni	60 ppm
S	4.5-6.0 %
N	0.5 %
Ash	0.6 %
O	1.1 %
H	10.3 %
C	83.3 %
Cu	5 ppm

Table 7. Bitumen composition

Component	Coke composition (%)
V	0.06-0.08
Ti	0.001-0.08
Ni	0.03-0.04
S	5-7
O	1-2
Ash	2.5-3
C	79-84
Water	7-10
Al	0.3
Fe	0.1-0.2
Si	0.2
Ca	0.07

Table 8. Suncor coke composition

Figures 3 and 4 illustrate the vanadium profile through the plant with the cyclotrells and electrostatic precipitators.[5] Table 9 shows the chemical analysis, provided by Suncor, of the ash collected from the ash pond with the cyclotrells installed and ash collected directly from the electrostatic precipitators. Currently ash is produced at a rate of approximately 78 tonnes/day containing 2.2% vanadium and 0.7% nickel.

Syncrude

The second plant, operated by Syncrude Canada Limited, commenced processing in 1978 and now has a production capacity of approximately 125,000 bbl/day. The processing of the oil sands to produce bitumen is essentially the same as the Suncor plant. However, the lower grade of oil sand requires flotation treatment of a middlings stream from the primary extraction stage to maintain a high recovery.

The bitumen is fed to a fluidized bed coker as shown in Fig. 5.[1,7] The reactor operates at a temperature of 600°C and a pressure of 10-20 psig (69-138 kPa) with injected steam being used to control the particle size to less than 200 μm. Approximately 15% of the bitumen is converted to coke with one-third of the coke being burned to maintain the fluidized bed temperature. Excess coke is produced at a rate of approximately 2,200 tonnes/day containing 9% sulphur, 0.07-0.09% nickel and 0.17-0.27% vanadium.

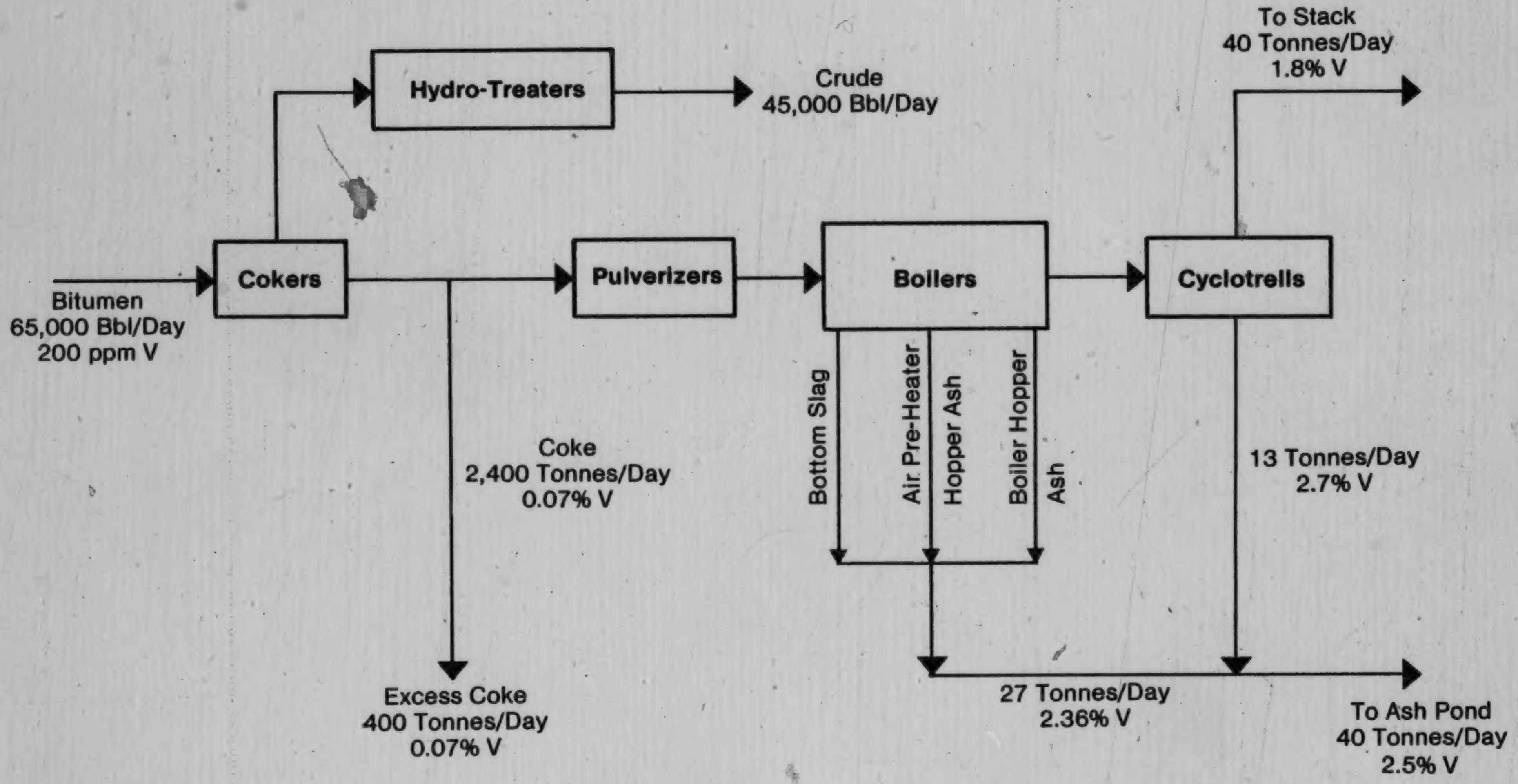

Bitumen
65,000 Bbl/Day
200 ppm V
Cokers
Hydro-Treaters
Crude
45,000 Bbl/Day
Pulverizers
Coke
2,400 Tonnes/Day
0.07% V
Excess Coke
400 Tonnes/Day
0.07% V
Boilers
Bottom Slag
Air Pre-Heater
Hopper Ash
Boiler Hopper
Ash
27 Tonnes/Day
2.36% V
Cyclotrells
To Stack
40 Tonnes/Day
1.8% V
13 Tonnes/Day
2.7% V
To Ash Pond
40 Tonnes/Day
2.5% V

Figure 3. Suncor plant vanadium profile with cyclotrells

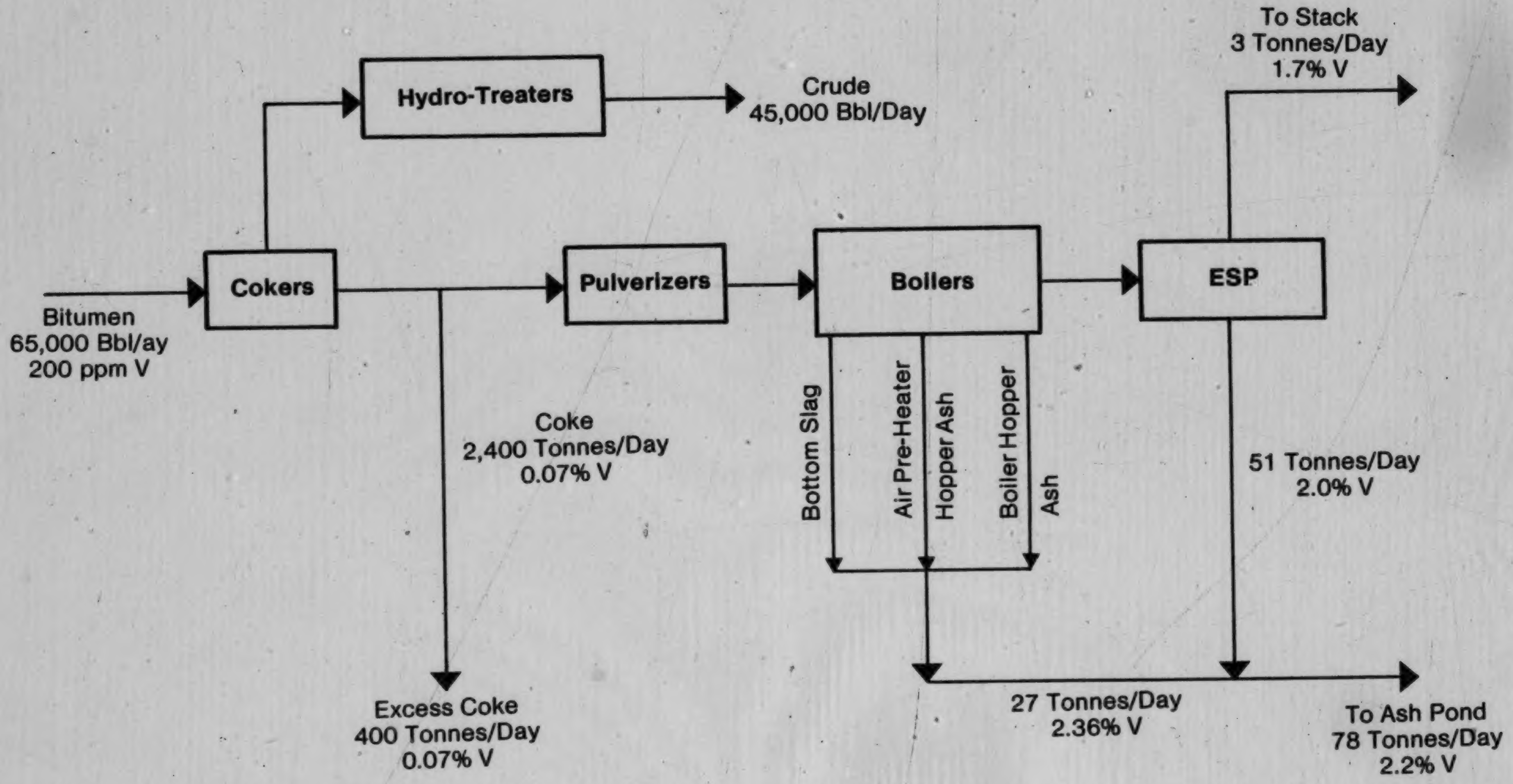

Hydro-Treaters
Crude
45,000 Bbl/Day
To Stack
3 Tonnes/Day
1.7% V
Cokers
Pulverizers
Boilers
ESP
Bitumen
65,000 Bbl/ay
200 ppm V
Coke
2,400 Tonnes/Day
0.07% V
Bottom Slag
Air Pre-Heater
Hopper Ash
Boiler Hopper
Ash
51 Tonnes/Day
2.0% V
Excess Coke
400 Tonnes/Day
0.07% V
27 Tonnes/Day
2.36% V
To Ash Pond
78 Tonnes/Day
2.2% V

Figure 4. Suncor plant vanadium profile with ESP

Compound	Cyclotrell ash(%)	ESP ash (%)
SiO_2	30	28.9
Al_2O_3	20	18.8
Fe_2O_3	6	5.5
V_2O_5	6	4.5
TiO_2	3	3.0
NiO	1.5	1.1
S	2	2.6
CaO	2	2.1
Na_2O	0.5	0.45
C	30	30
MoO_3	0.05	0.15
MnO	0.2	0.2
K_2O	1.6	1.1
MgO	1.6	1.1
P_2O_5	0.1	0.1

Table 9. Suncor ash composition

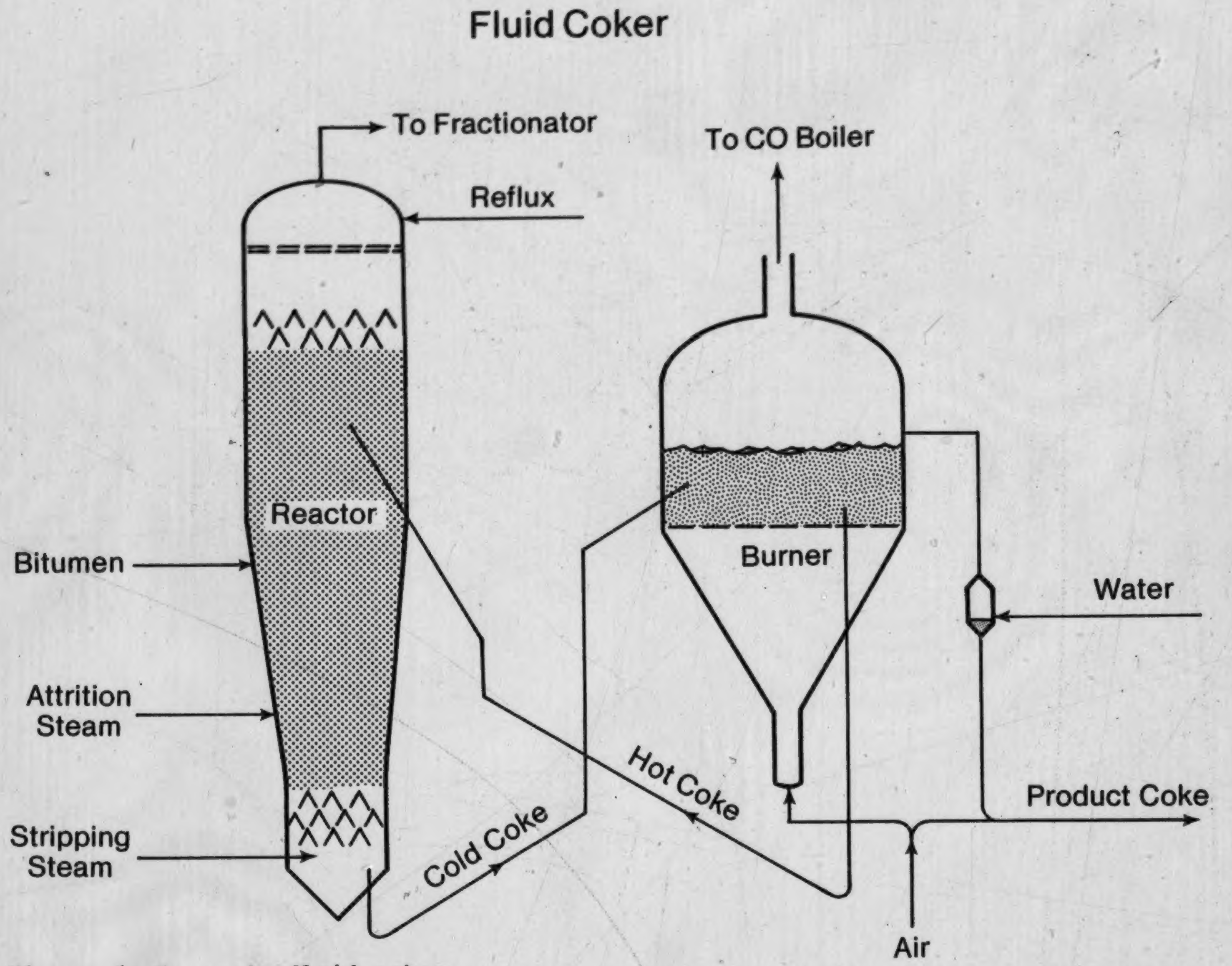

Fluid Coker
To Fractionator
Reflux
To CO Boiler
Reactor
Burner
Bitumen
Attrition Steam
Stripping Steam
Water
Hot Coke
Cold Coke
Product Coke
Air

Figure 5. Syncrude fluid coker

Fluid coker burner off gas, having passed through a CO boiler, is treated in electrostatic precipitators. The ash, or unburnt coke, since the coke particles pass through the CO boiler without any significant combustion, is collected at a rate of approximately 170 tonnes/day. The ash, containing approximately 1% vanadium and 0.3% nickel, is sluiced with the excess coke and sent to settling ponds.

Vanadium and Nickel Extraction

No detailed information is available on the chemical extraction of vanadium and nickel from oil sands fly ash. Although a patent[138] has been issued for the extraction of vanadium from the ash with sulphuric acid, another study[5] reports that extraction is low and acid use high.

Stemerowicz et al.[139] examined the pyrometallurgical recovery of vanadium and nickel from GCOS (Suncor) fly ash. Their mineralogical examination showed the carbon to be present as coarse irregular grains; the metal content was contained in aluminosilicate spheres.

Initially, the carbon content of the ash was adjusted by roasting at 800°C for 18 hr or by flotation. Flotation using pine oil, kerosene and Dowfroth 250 produced a froth containing 84% carbon and a residue containing 0.2% carbon.

The pyrometallurgical studies were aimed at producing commercial ferrovanadium and ferronickel; three routes were attempted:

1. Smelting the ash with FeS to form an iron-nickel matte and a vanadium-rich slag, then smelting the slag with aluminium or silicon to form FeV. The matte contained 40% nickel; however, the high slag to matte ratio (20:1) trapped vanadium in the matte and nickel in the slag.

2. Smelting the ash with carbon to form FeNi and a vanadium-rich slag. The alloy was produced in a commercial grade but 24% of the nickel was trapped in the slag.

3. Reducing the nickel, iron and vanadium with carbon to form an alloy and selectively reoxidizing to produce FeNi and a vanadium-rich slag. The initial alloy was produced with small metal losses to the slag, but the small mass produced (2% of the ash) limited the reoxidation step to one test.[140] The reoxidation products were

slag: 28% V, 24% Fe, 2% Ni

metal: 9% V, 74% Fe, 13% Ni

with the contamination possibly being due to a very thin slag layer. Further studies may be warranted when sufficient alloy can be produced for a comprehensive series of tests.

Two studies[141] [142] have examined the leaching of iron, vanadium and nickel from three types of Athabasca coke; delayed, fluid and flexicoke (from a pilot plant operation[143]). Sulphuric acid leaching removed 42% of the iron from the delayed coke and 30-40% of the three elements from the flexicoke, but little else. Bacteriological leaching with thiobacillus thiooxidans produced similar results. Halogenation with chlorine and bromine extracted less than 7% of the vanadium and 3% of the nickel.

The authors show that the vanadium in the fluid coke is concentrated at the centre of the coke spheres. They suggest that the leaching from flexicoke is due to its high porosity. Further, they state that coke combustion below 500°C leaves nickel and vanadium in an acid soluble form, but no results are presented.

A recent publication[144] has reported the first detailed physical and chemical examination of GCOS fly ash. A scanning electron microscope analysis of the ash showed that it consists of large coke particles (>37 μm), and fly ash spheres, cenospheres and pleurospheres. Microcrystals, 0.1-0.3 μm in diameter and 0.5-5 μm in length, were located on the surface of the spheres and appear to be enriched in vanadium, nickel, titanium and iron, and deficient in silicon. These microcrystals were the only component of the finest size fraction separated (<4.2 μm), and accounted for 7.6 wt % of the ash.

A procedure developed at the Alberta Research Council[145] is aimed at fixing the sulphur in the inorganic fraction of the Suncor coke. It produces an ash in which the vanadium and nickel are easily soluble in acid, although the metal concentration in the ash is significantly lowered.

II. ASH CHARACTERIZATION

A. PHYSICAL CHARACTERIZATION

Fly ash was supplied by Suncor (GCOS) and Syncrude throughout this project. The nomenclature used to identify the samples, date received and collection equipment are detailed as:

Suncor I	July 1977	Cyclotrell
Suncor II	August 1979	Cyclotrell
Suncor III	March 1980	Cyclotrell
Suncor IV	May 1980	ESP
Syncrude I	December 1978	ESP
Syncrude II	May 1980	ESP

All physical studies were carried out on fly ash (boiler and cyclotrell ash in Fig. 3) supplied by GCOS in July 1977. Preliminary studies showed that the ash had a density of 2.24 g/cm^3 determined by an air pycnometer and a mean particle diameter, using a Coulter Counter Particle Size Analyzer, of 15.7 μm.

Further particle sizing was carried out using a Warman Cyclosizer with a 20 g ash loading, a flow rate of 13.3 l/min, an elutriation time of 45 min and assuming a constant particle density of 2.24 g/cm^3. This sizing produced six fractions, each of which was then sized on the Coulter Counter to determine the mean particle diameter of each fraction, independent of particle density. The weight distribution, mean particle size and density of each fraction are shown in Table 10. In general terms, it can be noted that the material is very fine with 38.6 wt % of the ash particles being less than 14.5 μm in diameter.

Magnetic treatment of the ash produced a magnetic fraction of approximately 1%.

The Syncrude II ash has no magnetically separable fraction. It is also considerably coarser than the Suncor ash with 50% of the ash being >250 μm in diameter and only 10% being <100 μm.The density of the ash is 1.56 g/cm^3.

Cyclosizer Range (µm)	wt. %	Mean size (µm)	Density (g/cm^3)
> 51.3	3.4	-	1.95
38.2-51.3	6.6	44.8	2.13
25.6-38.2	15.2	33.0	1.98
18.3-25.6	23.5	21.0	2.02
14.5-18.3	12.7	15.5	2.02
< 14.5	38.6	4.2	2.49

Table 10. Particle size and density of Suncor I ash

B. CHEMICAL CHARACTERIZATION

Experimental

Chemical characterization of the ash involved six methods: atomic absorption analysis of digested ash solutions, neutron activation analysis, x-ray diffraction, electron spin resonance spectroscopy, Leco sulphur analysis and gravimetric silica determination.

Atomic Absorption

The standard technique for ash analyses recommended by Perkin-Elmer[146] was used for all ash samples received and for all treated ash samples. Approximately 0.1 g of ash was heated with 10 ml of hydrofluoric acid until near dryness. After cooling, 10 ml of perchloric acid was added and the solution steamed for 2 min. Then, after cooling again, a few drops of concentrated HCl were added and the solution heated until near dryness. If no undissolved ash remained, the solution was mixed with 15-25 ml of 10% HCl and made up to 100 ml with distilled water and 5 ml of 4% lanthanum chloride solution to reduce ionization interferences. To dissolve any remaining ash the perchloric acid addition was repeated.

The solution was then diluted as required and analyzed for various elements on a Pye Unicam SP 1950 Atomic Absorption Spectrophotometer using the methods recommended by Perkin-Elmer.[146]

The determination of vanadium by atomic absorption spectroscopy (AA) can be affected by the presence of titanium and aluminium in solution. Under the analytical conditions used for this study, these elements had a negligible effect on the apparent vanadium concentration at levels below 50 ppm. The vanadium absorption appeared to increase by 10% as the titanium and aluminium content increased from 50 ppm to 500 ppm.

The vanadium standards used in the AA analysis did not contain aluminium and titanium, since the content of these metals in the analyzed samples was unknown. The effect of using these AA standards, on results which are presented later, can be summarized for each section:

1. Ash Characterization:

The maximum aluminium and titanium concentrations in the ash characterization solutions are 10 ppm and 5 ppm respectively, producing a negligible change in the vanadium analysis.

2. Preliminary Extraction Studies:

The maximum aluminium and titanium concentrations are unknown. But any enhancement would increase the apparent vanadium extraction by a maximum of approximately 10%, so extraction processes are not disregarded due to analytical errors.

3. Vanadium Extraction Optimization:

The aluminium and titanium concentrations of solutions for vanadium analysis do not exceed 1 ppm - again, negligible effect.

4. Nickel Extraction Optimization:

The aluminium and titanium concentrations of solutions for vanadium analysis are approximately 75 ppm and 10 ppm respectively. Assuming the worst situation in that aluminium enhances vanadium concentration by a linear relationship from 50 ppm to 500 ppm aluminium, at which time the vanadium absorption has been enhanced by 10%; then the vanadium concentration and hence the vanadium extraction is estimated to be enhanced by no more than 2%. An extraction solution for this system was examined, and the addition of 500 ppm aluminium and titanium to the sample and standards changed the vanadium concentration from 13.3 ppm to 13.0 ppm, an error of less than 2%.

An alternative digestion procedure(4) produced similar results to the Perkin-Elmer technique. About 0.2 g of ash roasted at 500°C was digested at 110°C in a Parr Teflon digestion bomb with 2 ml of aqua regia and 2 ml of hydrofluoric acid for 1 hr. After cooling, 1 g of boric acid was added to the solution which was then heated on a waterbath for 15 min. The cooled solution was then made up to 100 ml and analyzed by atomic absorption spectroscopy.

Neutron Activation

The accuracy of the above dissolution techniques was checked for vanadium by neutron activation analysis (NAA) as it has previously been noted(4) that volatile vanadium compounds may be lost during digestion and roasting. The analyses were carried out with the assistance of Dr. M. J. Apps at the University of Alberta Slowpoke Facility.

Preweighed standards (V_2O_5/SiO_2) and samples were irradiated in the reactor by a flux of 10^{11} n/cm.sec^2 for 30 sec, then allowed to decay for 10 sec. The 1.433 MeV γ-ray emissions from the $^{51}V(n,\gamma)^{52}V$ reaction were then detected and counted by a Ge(Li) detector and a multichannel counting device.

X-Ray Diffraction

In an attempt to identify the mineral species present in the ash samples and in the ash after different treatment schemes, x-ray diffraction was carried out. The diffraction apparatus consisted of a Rigaku-Denki High Voltage Generator, a Philips Horizontal Goniometer and a Philips Curved Crystal Monochromator. The incident radiation was from a cobalt tube and the diffraction scans were made from 6 to 100 degrees (2θ).

Electron Spin Resonance

The electron spin resonance (esr) of various ash samples was determined with the assistance of Dr. K. Schultz at the Alberta Research Council.

The samples were placed in a high-intensity magnetic field and the frequency varied. To yield an esr spectrum the material must have one or more unpaired electrons. The magnitude of the resonant frequency can indicate the ion and compound present.

Sulphur Determination

Sulphur content was determined with a Leco Induction Furnace and Titrator. This technique assumes all of the sulphur is converted to sulphur dioxide which reacts with the free iodine to form HI.

$$SO_2 + I_2 + 2H_2O \rightarrow H_2SO_4 + 2HI$$

The presence of free iodine with a starch indicator is denoted by a blue colour and a standard potassium iodate solution is added according to the reaction,

$$KIO_3 + 5KI + 6HCl \rightarrow 6KCl + 3I_2 + 3H_2O$$

to maintain a constant colour intensity as detected by a photocell.

To obtain an adequate combustion of the sample in a short enough period of time to prevent crucible destruction, it was necessary to add one scoop of vanadium pentoxide, one scoop of iron and one scoop of tin to the ash sample. (One scoop = 0.5 cm^3). Normally, 1 g of sample will be suitable for a sulphur range of 0-0.2%; but for the high sulphur ash the samples weighed 0.25-0.4 g and the concentration of the iodate solution was increased by a factor of five.

Silica Determination

The silica content of the ash was determined by the technique of Rigg and Wagenbauer.[148] Briefly, 1 g of ash was fluxed with 5 g of sodium carbonate for 30 min. The cake was reacted with 25 ml of 9 M HCl, then heated to dryness. The salts were dissolved in 10 ml of concentrated hydrochloric acid followed by 100 ml of hot water. After filtering, the solid residue and filter paper were combusted in a platinum crucible and heated at 1200°C for 2.5 hr. After cooling and weighing, the silica residue was contacted with 15 ml of hydrofluoric acid and heated to dryness to drive off the silicon as SiF_4. Finally, the crucible was reheated to 1200°C for 30 min and then reweighed. The weight loss represents the silica originally present in the crucible; some additional silica dissolves in the initial treatment steps and can be determined by atomic absorption analysis of the filtrate.

Ash Composition

The elemental composition of the as-received fly ash is shown in Table 11. The variations in the Suncor I ash were determined during the use of a five gallon container of ash. The other Suncor and Syncrude ashes were sampled as a single batch.

For the Suncor ash, the carbon content ranges from 35.0% to 88.4% with the sulphur content being 2-5%. The Syncrude ashes have much higher carbon and sulphur contents,

Element	Syncrude		Suncor			
	I	II	I	II	III	IV
V	1.21	0.31	1.35-2.39	1.75	0.37	2.06
Ni	0.36	nd	0.43-0.68	0.67	0.21	0.69
Fe	2.13	0.87	2.23-3.44	3.38	0.81	2.86
Al	5.09	1.09	4.61-8.04	9.35	0.21	8.28
Ca	0.04	0.15	0.07-0.27	0.11	0.03	0.09
K	0.37	0.12	0.25-0.82	0.53	0.14	0.53
Mg	0.23	0.08	0.32-0.40	0.46	0.01	0.69
Mn	0.06	0.03	0.08-0.09	0.09	0.02	0.09
Mo	0.17	0.03	0.10-0.15	0.09	0.03	0.20
Na	0.90	1.20	0.83-2.85	2.48	0.37	5.45
Cu	0.04	0.04	0.04-0.05	0.04	0.03	0.04
Zn	0.03	0.02	0.03	0.03	0.02	0.03
Ti	0.94	nd	0.94-1.90	1.81	0.16	1.44
Si	0.2	0.8	10.3-16.0	26.1	3.0	12.9
C	72.7	84.1	50.5-54.5	35.0	88.4	40.4
S	8.13	7.78	2.65-3.47	1.90	4.35	2.41

nd: not detected

Table 11. As received fly ash composition (%)

as they are really unburnt coke.

Table 12 shows the carbon/sulphur free (<0.1% S) analyses of the ashes for vanadium, nickel, iron and titanium. For the Suncor ash, the ranges are:

Iron: 5.00-11.17%

Nickel: 1.02-2.90%

Vanadium: 2.78-5.10%

Titanium: 2.21-4.06%

Compounds are well-known that contain vanadium in the +2, +3, +4 or +5 oxidation states. Elemental vanadium has the electronic configuration:

$1s^2 2s^2 p^6 3s^2 p^6 d^3 4s^2$

Therefore, vanadium in the +2 or +4 oxidation states as well as elemental vanadium, has unpaired electrons and will produce an esr spectrum.

The esr spectrum of Suncor I ash contained no vanadium resonance peaks, only the characteristically broad peaks of magnetite, Fe_3O_4. Thus the vanadium in the Suncor I sample is present in the +3 and/or +5 oxidation states and the magnetically separable fraction is probably magnetite.

The x-ray diffraction scans of all the ashes produced broad peaks at 6-30 degrees (2θ), typical of amorphous silicate material, and a few small unidentifiable peaks at higher angles. Scans of the various Suncor I ash size fractions produced by the cyclosizer were similar, although the peak intensity increased with decreasing particle size. This result may be due to an increasing compound

Element	Syncrude		Suncor			
	I	II	I	II	III	IV
V	6.31	3.83	3.21-5.10	2.78	5.10	3.60
Ni	1.87	0.20	1.02-1.45	1.06	2.90	1.21
Fe	11.11	10.74	5.31-7.34	5.35	11.17	5.00
Ti	4.90	nd	2.24-4.06	2.87	2.21	2.52

nd: not detected

Table 12. Carbon/sulphur free ash composition (%)

concentration, or, more probably, due to a particle size effect.

Additional samples of the Suncor I ash were roasted in air, argon and hydrogen at temperatures of 700°-1100°C. Although 4 or 5 well defined peaks were produced in most of the scans, they were insufficient for any mineral species identification from the ASTM X-Ray Powder Data File.

Particle Size Effect

Previous authors[1-21] have noticed that the concentration of various elements in a fly ash is dependent upon the particle size of the ash. Specifically, one group[14] have noted that vanadium, nickel, titanium and iron are enriched in the fine fraction (<4.2 μm) of GCOS fly ash.

Table 13 shows the results of chemical analyses of various size fractions of Suncor I ash. In general terms, it can be noted that:

a. The concentration of Cr, Fe, K, Mn, Ni, Ti and V increases as the particle size decreases.

b. The maximum concentration of Al, Mg and Si occurs in the 14.5-18.3 μm fraction.

c. Compared to the bulk material, the fine fraction is deficient in Al, C, S and Si; and enriched in Ca, Cr, Fe, K, Mg, Mn, Na, Ni, Ti and V.

d. Carbon and sulphur concentrations decrease as particle size decreases.

Size (μm)	wt. %	Al	C	Ca	Cr	Fe	K	Mg	Mn	Na	Ni
> 51.3	3.4	1.76	80.8	0.20	0.02	1.31	0.43	0.21	0.08	0.36	0.14
38.2-51.3	6.6	1.62	80.0	0.43	0.02	1.35	0.44	0.27	0.07	0.35	0.17
25.6-38.2	15.2	3.47	69.2	0.82	0.02	2.37	0.47	0.29	0.09	0.38	0.32
18.3-25.6	23.5	5.37	48.6	1.26	0.03	3.30	0.91	0.95	0.11	0.85	0.57
14.5-18.3	12.7	6.90	38.2	1.10	0.08	4.35	1.19	1.07	0.13	0.75	0.86
< 14.5	38.6	3.92	22.6	0.57	0.10	5.28	1.28	0.80	0.15	0.80	1.00
Suncor I	100	6.19	47.8	0.38	0.05	3.66	1.05	0.54	0.13	0.57	0.68

Table 13. Composition of Suncor I ash size fractions (%)

Size (µm)	wt. %	S	Si	Ti	V(AA)	V(NAA)
> 51.3	3.4	3.88	4.28	0.73	0.76	0.78
38.2-51.3	6.6	3.95	3.53	0.90	0.85	0.84
25.6-38.2	15.2	3.51	5.95	2.05	1.24	0.96
18.3-25.6	23.5	2.60	15.6	2.71	1.97	1.87
14.5-18.3	12.7	1.81	16.2	3.56	2.79	2.38
< 14.5	38.6	1.08	8.58	4.24	3.16	-
Suncor I	100	2.65	10.3	2.90	2.39	2.56

Table 13. Composition of Suncor I ash size fractions (%) (continued)

Now, according to the simplified vaporization-condensation model and its associated concentration equations, if the deposition layer is assumed to be of negligible thickness,

$$C_a \quad C_m \quad \frac{6\,C_s}{D}$$

Thus, $C_a \propto D^{-1}$, and a plot of C_a vs. 1/D will have a slope of $6C_s/\rho$ and an intercept at C_m.

These plots are presented in Fig. 6 and 7 for vanadium and nickel. The results are similar to those of Smith et al.[18] described earlier with a linear portion over the coarse size range and a relatively constant concentration region in the finer size range.

Evaluating the parameters and assuming $\rho = 2.24$ g/cm³;
for vanadium $C_s = 1742$ ug/cm² and $C_m = -0.26\%$,
for nickel $C_s = 666$ ug/[illegible]nd $C_m = -0.23\%$.
However, these results may be in error due to the negative values of C_m and the high vanadium value of C_s, (which implies that all the spheres consist entirely of vanadium).

The basic reason for these possibly erroneous results is that the carbon content is not distributed evenly throughout the ash. Its presence in the sized ash decreases as the particle size decreases and, as will be shown in the next section, it is present as discrete material, separate from the other fly ash components. Thus, if there is negligible metal content in the carbon grains, carbon-free

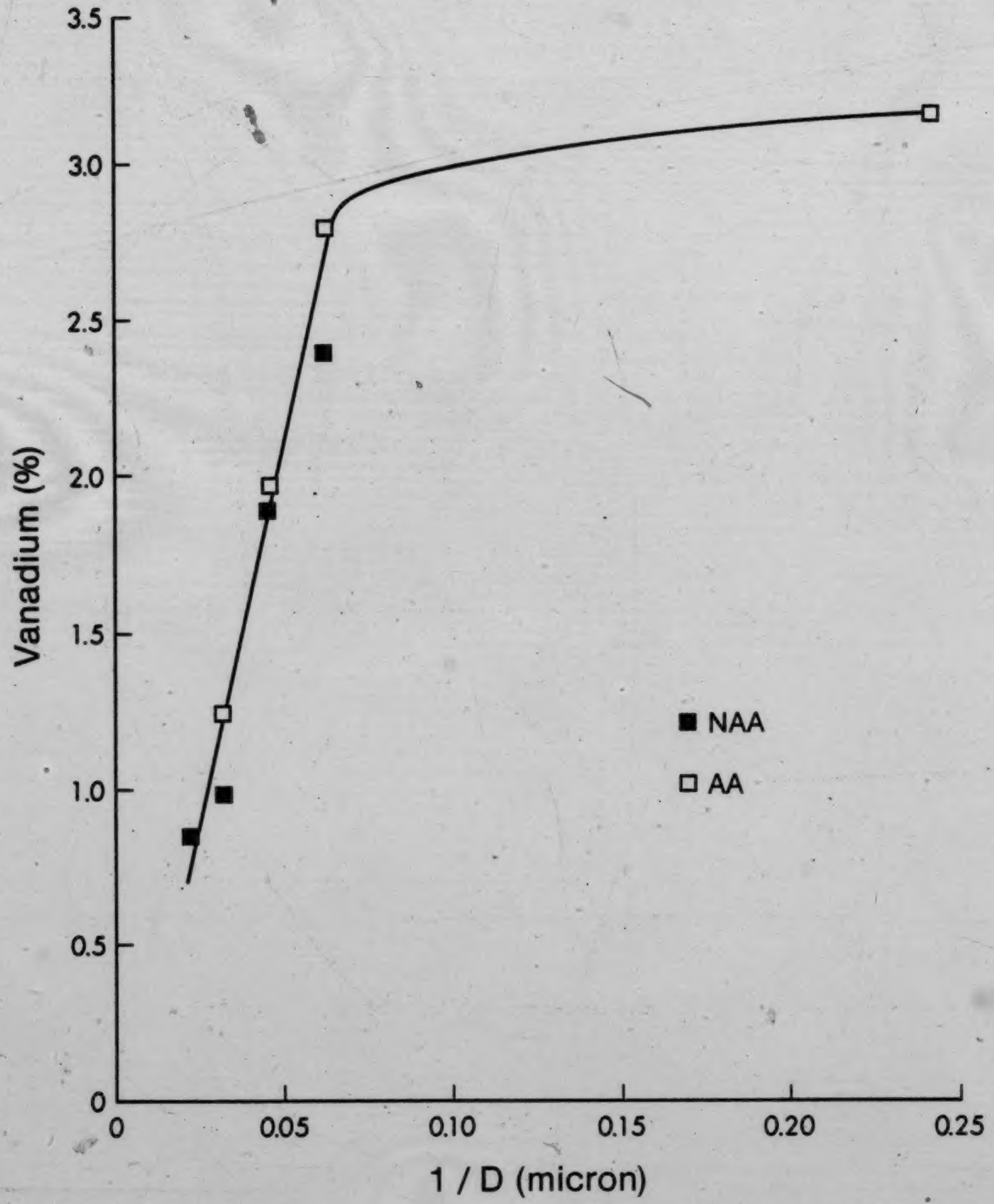


Figure 6. Dependence of vanadium concentration on ash particle diameter (D)

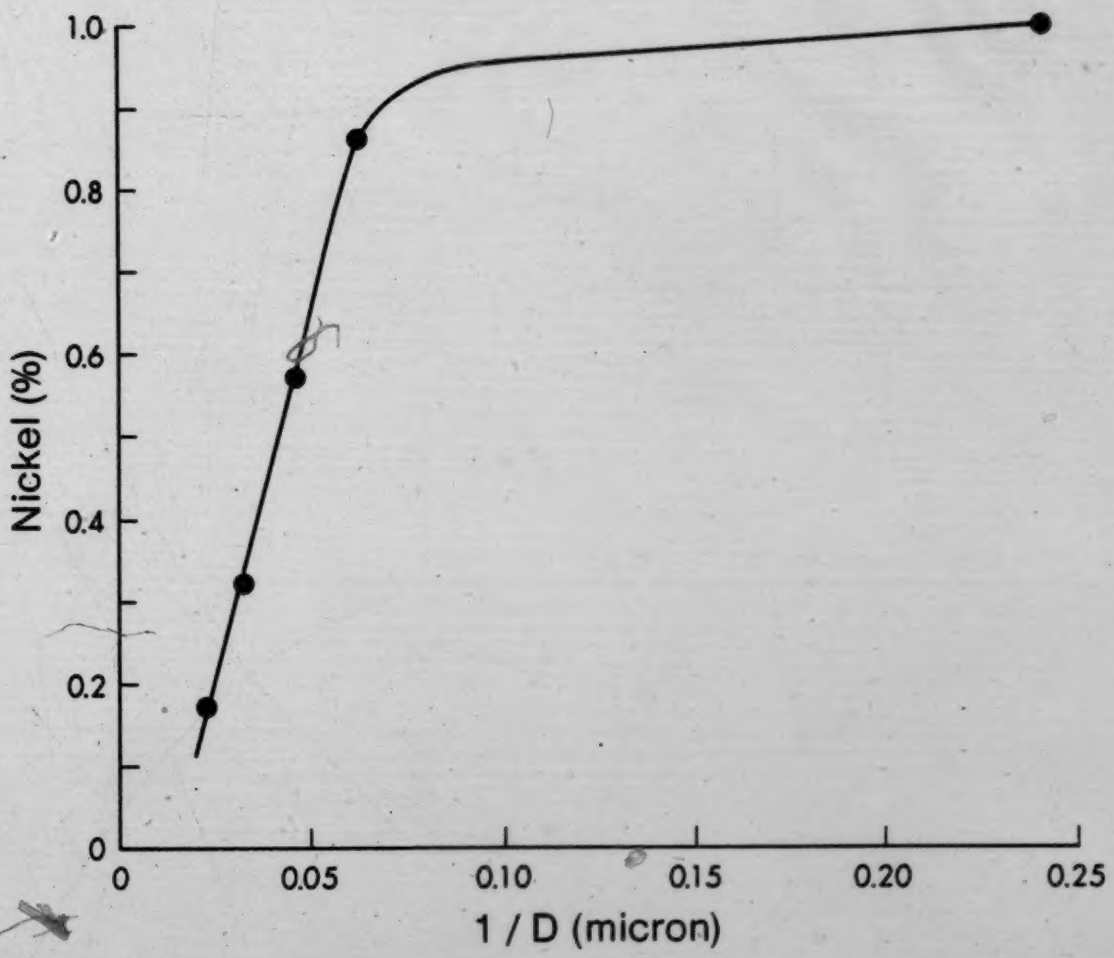


Figure 7. Dependence of nickel concentration on ash particle diameter (D)

analyses of the ash must be used when considering elemental trends.

The treatment of this problem by other researchers[9-21] during the examination of concentration trends is not reported, except for four cases:

a. Kaakinen et al.[15] used carbon-free ash,

b. Smith et al.[10] used ash with only 0.3% carbon, which does not significantly affect the trends,

c. Davison et al.[18] would have shown extra concentration-size trends for vanadium and beryllium, if they had studied the ash on a carbon-free basis.

d. The only study of GCOS ash[144] used carbon-free material.

If the metal content of the carbon grains is similar to the silicate ash, the vaporization-condensation equation may still be valid.

Table 14 shows the element concentrations of various size fractions of Suncor I ash on a carbon-free basis. Although no trends are now apparent, it is worth noting that the "matrix" elements (Al, Ca, Mg, Na and Si), are generally at a lower concentration in the fine ash (<14.5 μm) than the other size fractions.

The lack of concentration trends implies that the vaporization-condensation model is not applicable to the conditions under which Suncor fly ash is produced. In particular, these results suggest that V_2O_5 is not vaporized

Size fraction (µm)	Al	Ca	Fe	Mg	Na	Ni	Si	Ti	V(AA)	V(NAA)
> 51.3	9.2	1.0	6.8	1.1	1.9	0.7	22.3	3.8	4.0	4.1
38.2-51.3	8.1	2.2	6.8	1.4	1.8	0.9	17.7	4.5	4.3	4.2
25.6-38.2	11.4	2.3	7.8	1.0	1.3	1.1	19.6	6.7	4.1	3.2
18.3-25.6	10.4	2.5	6.4	1.8	1.7	1.1	30.4	5.3	3.8	3.6
14.5-18.3	11.2	1.8	7.0	1.7	1.2	1.4	26.2	5.8	4.5	3.9
< 14.5	5.1	0.7	6.8	1.0	1.0	1.3	11.1	5.5	4.1	-

Table 14. Carbon free composition of Suncor I ash size fractions (%)

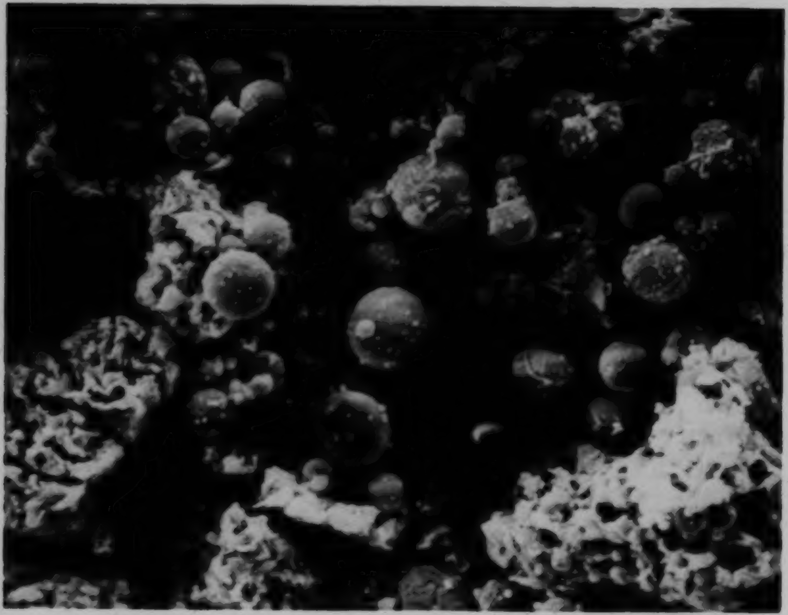
during coke burning. Since the boiling point of V_2O_5 is significantly above the firing temperature of the coke, little vaporization may be expected.

The lack of volatilization of vanadium is suggested by a study of the utilization of Suncor coke as fuel in cement manufacture[149] which showed that only 5% of the vanadium is collected in cement kiln off-gas during combustion at 1450°C.

SEM Studies

Microscopic analysis of the fly ash was carried out using an International Scientific Instruments ISI-60 scanning electron microscope (SEM) with an energy-dispersive analyzer (EDA), which can present information on the elements in the sample. Although only semi-quantitative, the qualitative results can be an indication of the relative proportions of elements present in the ash. The energy dispersive analyzer uses an electron beam which determines the elemental composition of 1 μm^3 of sample. Thus, the beam may penetrate thin samples and the reported composition may include the material beneath the sample. The markers at the upper left corner of the SEM photographs indicate the scale. To simplify the use of the markers, the length of the farthest right marker is included after the photograph title.

Suncor I ash, typical of all the Suncor samples, is shown in Photograph 1. The ash basically consists of two



Photograph 1: Suncor I ash (10 μm)

Photograph 2: Suncor ash cenosphere (1 μm)

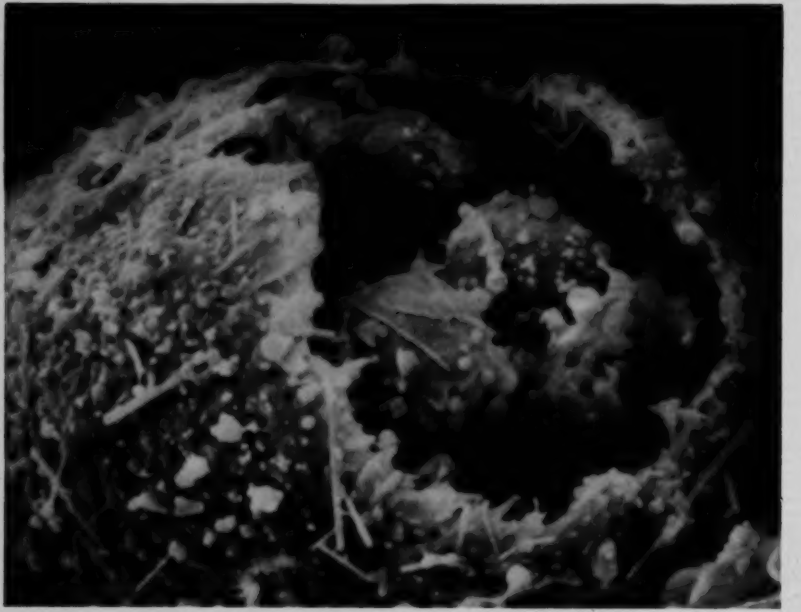
forms, ash spheres and irregular carbon grains.

The spheres are generally very regular, and consist of single spheres with a clean surface, ones with microspheres attached to the surface and agglomerations of spheres. It is expected that some of the spheres are hollow (cenospheres), similar to the sphere shown in Photograph 2, which has a small opening. The other fly ash phenomenon of pleurospheres was not unequivocably found, but it would have been very fortunate to have done so; one would need to locate a sphere similar to Photograph 2 and, within it, identify a sphere larger than the visible hole.

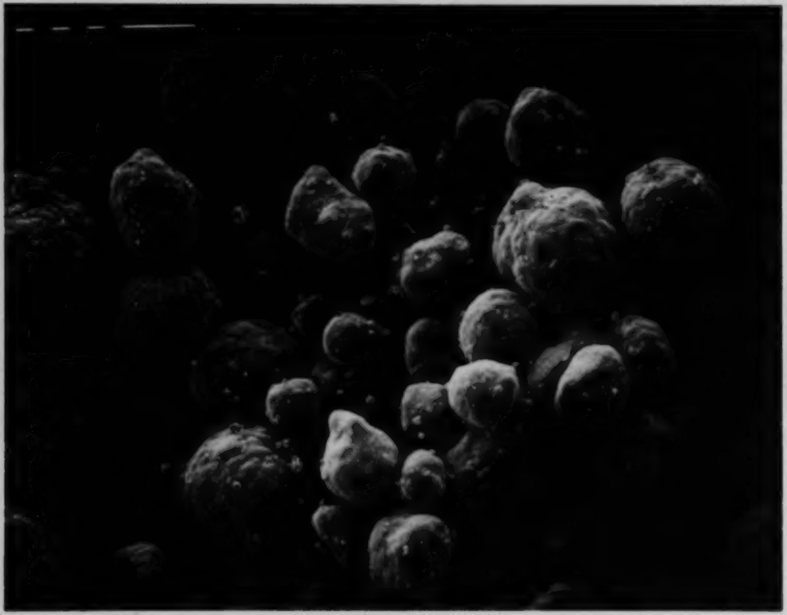
Photograph 3 may show a pleurosphere, but it is more probably a large broken cenosphere that has physically entrapped smaller spheres. The sphere is covered with small microcrystals, 0.1-0.8 µm in diameter and 0.5-5 µm in length, similar to those identified by Bueno et al.[144] The microcrystals were found very infrequently in all of the available ash samples, which differs markedly from the high concentration of crystals (>7 wt %) found in the above study.

EDA examination of the individual crystals showed them to be rich in titanium, vanadium or iron, or some combination of these elements. But there was no apparent difference between those rich in vanadium and those rich in iron etc.

The elemental EDA scans of fly ash spheres and microcrystals are presented in Fig. 8. (The gold peaks are



Photograph 3: Suncor ash microcrystals (1 μm)



Photograph 4: Syncrude II ash (100 μm)

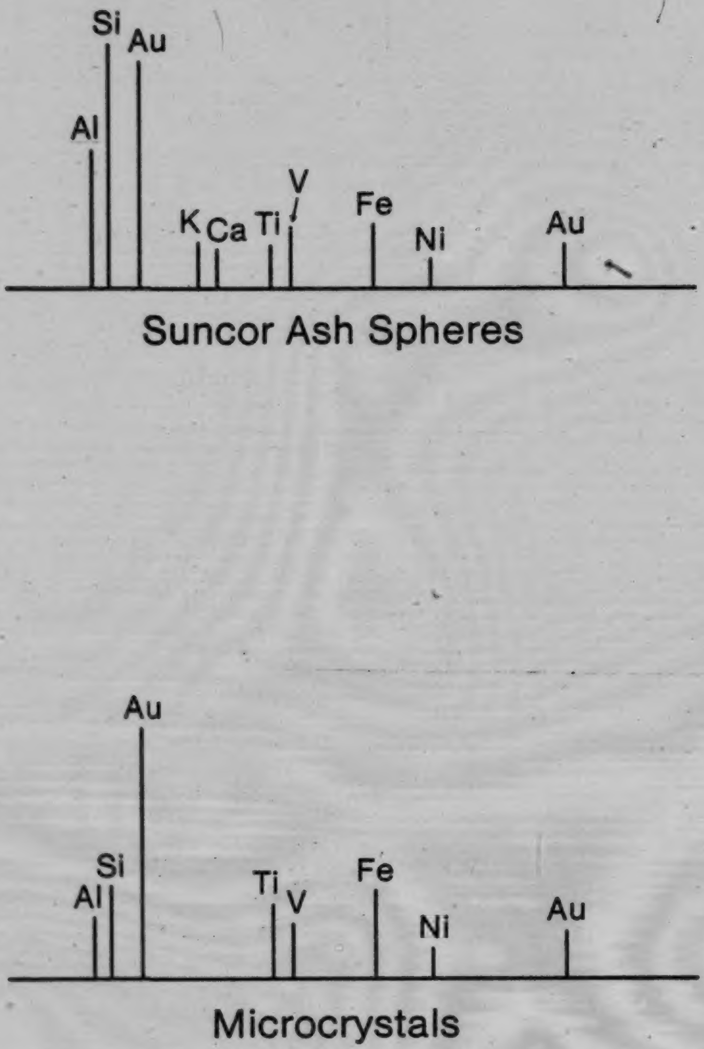


Figure 8. EDA representation of Suncor ash spheres and microcrystals

from the sample preparation routine.) These scans may show that the crystals are relatively rich in iron, vanadium, titanium and nickel compared to the fly ash spheres. Additionally, the crystals are deficient in aluminium, silicon, calcium and potassium compared to the bulk material. These results are similar to those of Bueno et al, which suggested that the concentration of vanadium, nickel, iron and titanium are increased, and silicon decreased in the crystals.

Furthermore, they report the "fines" (<4.2 μm) as being only microcrystals. Although the lack of suitable equipment prevented the extraction of a similar sample from Suncor ash, it was noted that there was an increased quantity of microcrystals in the fine ash (<14 μm).

Syncrude II ash is shown in Photograph 4. The grains mainly consist of carbon with small amounts of silicon and aluminium spread throughout.

III. PRELIMINARY EXTRACTION STUDIES

The initial aim of the preliminary extraction studies was to use the information gained from the ash characterization to suggest a possible route to extract vanadium and nickel from the ash. However, the characterization provided insufficient detail of the compounds present in the ash to reduce the number of preliminary tests. Similarly, the literature review produced an extremely wide range of possible extraction procedures. Thus, the preliminary extraction studies were carried out in an attempt to select the optimum procedure from a large number of possibilities.

A. DIRECT LEACHING

Direct leaching of vanadium and nickel from ash has previously been achieved by a variety of reagents.[32-56] The majority of these techniques were applied to the Suncor I fly ash.

The general leaching conditions were such that 20 g of ash was leached with 60 ml of 10% reagent for 4 hr at 94°-97°C with mixing under reflux conditions. The hot slurries were filtered and the filtrate analyzed, after cooling, by atomic absorption spectroscopy for vanadium, nickel and iron. Occasionally throughout the leaching studies the residue was dissolved and analyzed. The mass balance was accurate to within ±5%.

The leachants used and variations in the leaching conditions were as follows:

a. water at 20° and 97°C.

b. nitric, hydrochloric and sulphuric acids at 10% concentrations; equivalent to molarities of 1.67, 2.87 and 1.09, respectively.

c. 10% solutions of sodium carbonate, sodium hydroxide and ammonia (as NH_4OH) with molarities of 1.04, 2.77 and 5.62, respectively.

d. hydrogen peroxide: 5% solution at 25°C and 5% solution at 25°C acidified to pH 1.5 with sulphuric acid.

e. 10% sulphuric acid with 10% sodium chloride; 5% sulphuric acid with 5% hydrochloric acid.

The results of these leaching tests for the extraction of vanadium, nickel and iron are shown in Table 15. Only the acidic extractions were affected by increasing the leaching time to 12 hr; the increased extractions were:

HNO_3 - V:13.5 to 18.8%, Ni: 7.9 to 12.2%
HCl - V:13.9 to 19.9%, Ni:12.2 to 20.4%
H_2SO_4 - V:17.3 to 18.8%, Ni:11.8 to 16.3%

Thus, increasing the leaching time does not produce a sufficiently increased recovery to merit further studies.

Table 15 also shows that the simple procedure of leaching with water will not extract any significant quantities of vanadium, nickel or iron. However, water leaching at room temperature will dissolve some elements, namely:

30-40% of the calcium, copper and sodium,
20-25% of the chromium and magnesium, and
15-20% of the manganese and potassium.

These extraction results, along with the proven increase in extraction of some metals from oil sand cokes with the bacteria thiobacillus thiooxidans,[142] may indicate possible industrial environmental problems from groundwater contamination.

It is impossible to accurately interpret the variations in extraction efficiency; however, a few comments can be made. Firstly, acidic solutions dissolve up to 20% of the three metals examined. Secondly, basic solutions, apart from the high extraction of vanadium by sodium hydroxide,

Leachant and Conditions	Extraction V	Ni	Fe
H_2O 20°C	0.4	0.7	nd
H_2O 97°C	0.2	2.3	nd
H_2SO_4	17.3	11.8	14.3
HCl	13.9	12.2	16.6
HNO_3	13.5	7.9	9.8
NH_3	4.5	nd	nd
NaOH	27.2	0.2	0.1
Na_2CO_3	6.7	nd	nd
H_2O_2	1.8	37.1	nd
H_2O_2 (acid)	8.5	2.8	16.8
H_2SO_4/HCl	20.4*	2.2*	7.3*
H_2SO_4/NaCl	20.4*	14.1*	2.7*

*: Na_2SO_4 ppt. formed, nd: not detected

Table 15: Direct leaching extractions (%)

dissolve small or negligible quantities of the metals. Lastly, hydrogen peroxide, although dissolving a large quantity of nickel, is neither successful for vanadium extraction nor a likely economic industrial leachant.

Overall, none of the extraction results shows a sufficiently high recovery (>70%) under reasonable leaching conditions to merit further investigation.

B. PRE-LEACH ROASTING

Prior to leaching, the Suncor I ash was roasted in air in a muffle furnace for 6 hr at temperatures of 600°, 800° and 1200°C. At 1200°C the ash had completely melted.

The leaching conditions were similar to the previous tests with a phase ratio of 3 ml/g of roasted ash. Analysis of the leachates was obtained by atomic absorption spectroscopy. The extraction of vanadium, nickel and iron by the same reagents used in the previous tests is shown in Table 16.

Very little vanadium, nickel and iron dissolves in any of the leachants from ash that has been treated at 1200°C. The exception is the case of sodium hydroxide, where 40% of the vanadium is transferred into the basic solution.

Only small quantities of iron and nickel are dissolved by any reagents from ash roasted at 800°C. However, the acid leachants dissolve 45-57% of the vanadium; the basic ones, 20-38%. The acid extractions are similar to those found previously.[72] [73]

Roasting at a lower temperature (600°C) slightly decreased the extraction of vanadium by the two leachants tested (sulphuric acid and sodium hydroxide), and it may be expected that similar effects would be observed for the other leaching solutions. Further tests showed that roasting for longer time periods, or roasting in oxygen had a negligible effect on the extractions.

Leachant	Extraction and Roasting Temperature					
	V		Ni		Fe	
	800°C	1200°C	800°C	1200°C	800°C	1200°C
H_2O 97°C	5.7	0.4	nd	nd	nd	nd
H_2SO_4	54.0"	5.7	2.3"	1.6	4.6"	12.5
HCl	45.7	9.0	2.1	4.0	5.0	4.4
HNO_3	57.3	5.3	2.1	0.7	4.0	7.2
NH_3	20.2	0.7	nd	nd	nd	nd
NaOH	29.7	40.0	0.1	0.2	0.1	0.1
Na_2CO_3	38.4*	3.7	0.1*	0.1	nd*	nd
H_2O_2	27.1	nd	0.1	nd	nd	nd
H_2SO_4/NaCl	44.8	8.0	1.2	3.2	3.9	20.6

": $CaSO_4$ ppt. formed, *: Na_2SO_4 ppt. formed, nd: not detected

Table 16: Pre-leach roasting extractions (%)

Another series of tests involved roasting the ash at various temperatures followed by leaching with 10% sulphuric acid. The maximum extractions, which occurred after roasting at approximately 760°C, were 60% of the vanadium, 5% of the nickel and 6.8% of the iron.

During the series of tests shown in Table 16, precipitates were formed in the filtered solutions on cooling. These were identified by x-ray diffraction analysis as sodium sulphate and calcium sulphate.

Once again the results did not produce a sufficiently high extraction of vanadium or nickel to warrant further investigation.

Pre-leach roasting with various additives has been suggested as the best extraction route for many ashes.[35 58-72] Suncor I ash was roasted at 800°C with 20 wt % of each of the two most popular additives, sodium chloride and sodium carbonate. The leaching reagents and procedure were similar to the previous tests and the extraction results are presented in Table 17.

The vanadium extraction results were high compared to previous tests, producing solutions with negligible contamination by nickel or iron.

The highest vanadium extraction used sodium chloride as the additive and leached with sodium hydroxide solution. But, since water and the basic leachants also extracted a reasonable quantity of vanadium into solution, these cannot be disregarded and will be investigated further in the next

Leachant	**Extraction and Additive**					
	V		**Ni**		**Fe**	
	NaCl	Na_2CO_3	NaCl	Na_2CO_3	NaCl	Na_2CO_3
H_2O 97 C	68.8	68.0	nd	0.1	nd	nd
H_2SO_4	g	g	g	g	g	g
HCl	g	g	g	g	g	g
HNO_3	g	g	g	g	g	g
NH_3	58.6	40.1	nd	nd	nd	nd
NaOH	79.5	46.4	nd	0.1	nd	nd
Na_2CO_3	75.2	59.1	nd	0.1	nd	nd
H_2SO_4/NaCl	g	g	g	g	g	g

g: gelatinous product, nd: not detected

Table 17. Additive pre-leach roasting extractions (%)

section.

The formation of an unfilterable gelatinous product during the attempted leaching of the ash by acid solutions was found to occur until the acid concentration was substantially decreased. At a concentration of 3% sulphuric acid, the ash became filterable after leaching. This acid solution extracted 37% of the vanadium from sodium chloride roasted ash and 33.5% from sodium carbonate ash.

Gelatinous material produced by acid leaching is normally formed by activation of clay minerals which leads to an increase in their catalytic, adsorptive and decolourizing power. Ovcharenko et al.[150] have shown that activation is accompanied by the dissolution of the octahedrally coordinated magnesium, iron and aluminium ions. The transfer of these ions to the solution is accompanied by the transfer of protons into the structure to form Si-OH groups. When the dissolution occurs at the innermost octahedra, the silicon-hydroxide groups are no longer retained on the particle; they break away and polymerize to form silica gel.

Roasting with sodium chloride or sodium carbonate at 600°C and leaching with sodium hydroxide or 3% sulphuric acid reduces vanadium extraction by approximately 50%.

C. MISCELLANEOUS

Although these miscellaneous tests were not carried out in chronological order with the preceding and succeeding tests, the following series of studies may be considered as preliminary.

Chlorination

Direct chlorination of ash has been suggested in two studies[32] [66] while another study[88] has reported that roasting with sodium chloride will volatilize $VOCl_3$.

All vanadium chlorides are:

1. liquids or gases at room temperature,
2. in a gaseous form above 100°C, and
3. soluble in water or alkali.

These properties were utilized in the chlorination apparatus and experiments similar to those of Skeaff.[151]

The ash was heated to various temperatures (287°, 492° and 700°C) in an argon atmosphere. Chlorine gas was then introduced to 4 g ash samples at a rate of approximately 0.5 l/min for one hour. The furnace gas was passed through a trap at 0°C, then bubbled through a 250 g/l solution of sodium hydroxide which would absorb unreacted chlorine gas or volatile vanadium compounds. A second trap contained a solution of sodium hydroxide and silver nitrate, so that any chlorine reaching this stage would produce a visible precipitate of silver chloride as a protection against atmospheric venting of chlorine gas.

For each temperature, three "products" were analyzed: high temperature condensate after dissolution in sodium hydroxide solution, low temperature condensate after similar dissolution and the sodium hydroxide collector solution. The low temperature condensate was collected in the 0°C trap; the high temperature condensate in the silica tubing from the furnace to the trap. No vanadium, nickel or iron was carried through to the collector solution. The vanadium was recovered as low temperature condensate; the nickel as high temperature condensate. The iron was collected as a high temperature condensate at the lowest temperatures; but at 700°C, 83% of the recovered iron was low temperature condensate.

However, as shown in Table 18, the extraction recovery of the three elements is insufficient to warrant further investigation.

Smelting

The direct smelting of an ash to form an alloy has been suggested in Japanese patents[76] [77] and by Stemerowicz et al.[138] using GCOS (Suncor) fly ash. The latter study recommended a process of reducing the vanadium, nickel and iron with carbon to form an alloy and then selectively reoxidizing to produce ferronickel and a vanadium rich slag.

Based on this study, three smelting tests were carried out with carbon-free (roasted) Suncor I ash. The ash mixture consisted of:

Chlorination temperature (°C)	Extraction V	Ni	Fe
287	1.0	5.3	0.7
492	1.4	5.5	0.9
700	2.3	2.9	3.0

Table 18. Chlorination extractions (%)

100 g of roasted Suncor I ash,
26 g of sodium carbonate, and
coke as a reducing agent.

The sodium carbonate addition was enough to produce a slag with a silicate degree of approximately one, so as to avoid entrapping any alloy in a high viscosity slag.

Vanadium, nickel and iron were assumed to be present as V_2O_5, NiO and Fe_3O_4 respectively. If these compounds are reduced by carbon to the metal and carbon monoxide, 3.35 g of carbon are required; if reduced to metal and carbon dioxide, 1.67 g are required. The four test mixtures contained 2, 4, 15 and 20 g of coke (90% carbon); the last test also contained 4 g of calcium fluoride to increase slag fluidity. The earlier study[139] used a carbon to ash ratio of approximately 0.1 to 1. This implies that the carbon addition was four times the quantity of carbon required to reduce the metal oxides and form carbon monoxide.

The ash mixtures were placed in a covered zirconia crucible and heated in a furnace to 1400°C for 6 hr. After smelting, the volume had been reduced by 95% and the residue was firmly bound to the zirconia crucible. In each test the slag residue was broken and examined for areas of alloy entrapment.

The quantity of alloy formed, its metal content and the recovery of each metal in the alloy is shown in Table 19. The results of the study compare reasonably to the earlier work under the recommended optimum conditions.

Coke addition (g)	Alloy produced (g)	Alloy composition			Alloy recovery		
		Ni	V	Fe	Ni	V	Fe
2	0	-	-	-	-	-	-
4	0.12	17.1	9.3	71.6	2	1	2
15	11.62	14.8	14.9	59.4	82	77	88
20	7.68	10.7	22.9	44.2	81	55	63

Table 19. Smelting-alloy recovery and composition (%)

Even though the nickel and vanadium recoveries are reasonable, further processing must occur to separate the metals and produce commercial products. The production of FeV and FeNi from the alloy has only been briefly examined,[140] primarily due to the large quantity of ash required (100 kg of ash may only produce 2 kg of alloy).

In this study, the smelting technique was not examined any further due to the high recoveries of vanadium and nickel by other techniques and the materials handling problem involved in even a brief determination of the alloy product.

Pressure Leaching

An unpublished study[152] of the sulphuric acid pressure leaching of GCOS fly ash showed that the temperature (65°-120°C) and sulphur dioxide pressure (0-50 psig) have little effect on vanadium and nickel extraction. However, a high temperature leach (250°C, 550 psig) extracted 70% of the nickel and 32% of the vanadium.

An attempt was made to reproduce this high nickel recovery by leaching Suncor I ash at a temperature of approximately 130°C and a pressure of approximately 50 psig. The extraction test extracted 53.2% of the nickel and 26.5% of the vanadium.

Sulphidation

Sulphurization or sulphidation of ash has been reported as being successful[32] but no information is available.

The single test initially attempted with Suncor I ash involved roasting a mixture of the ash and 20 wt % sulphur at 900°C and leaching with 10% sulphuric acid. This preliminary test extracted 93.5% of the nickel and 25.6% of the vanadium which obviously merits further study.

Reduction Roasting

Direct reduction roasting was attempted by roasting Suncor I ash in a hydrogen atmosphere at 800°C. Subsequent leaching was achieved with 10% sulphuric acid and 10% sodium hydroxide solutions. The extractions, which were too low for further investigation, were:

H_2SO_4	3.4% vanadium, 0.1% nickel
NaOH	11.3% vanadium, 0.1% nickel

IV. OPTIMUM EXTRACTION ROUTES

A. VANADIUM

From the preliminary extraction studies, it appears that the highest vanadium extraction from Suncor I ash is obtained by roasting the ash with sodium chloride and subsequent leaching. This section of the study is aimed at optimizing the extraction conditions, mainly with regard to the following variables:

1. leaching medium
2. roasting temperature
3. sodium chloride additions
4. concentration/pH of leachant
5. leaching temperature
6. leaching phase ratio

The experimental conditions were similar to those previously used. Approximately 20 g of ash plus additive was roasted in a tube furnace in air, with the temperature controlled to ±5°C. Leaching was carried out at 97°C for 4 hr, with mixing under reflux conditions, and a phase ratio of approximately 3 ml/g of roasted ash. The hot slurries were filtered and the filtrate analyzed, after cooling, by atomic absorption spectroscopy.

Leachant

The preliminary tests showed that leaching of salt-roasted ash with water or sodium hydroxide produced a reasonable vanadium dissolution. Leaching with 10% sulphuric acid produced an unfilterable product; leaching with 3% sulphuric acid produced a low extraction. Thus the most effective leachant is either water (pH 6) or a basic solution.

Roasting Conditions

Prior to leaching with either water or 10% sodium hydroxide solution, the ash was roasted with 10 wt % sodium chloride for 4-6 hr at temperatures of approximately 700° to 1000°C. The effect of roasting temperature on the extraction of vanadium with the two leachants is shown in Fig. 9 and 10. (Appendix I presents the values upon which Fig. 9 and all future plots are based.)

As the best extractions are similar, the use of water as the leaching agent is economically more beneficial. The roasting temperature to maximize leaching recovery in the water leaching system was found to be 905°C.

Extending the roasting time beyond 6 hr does not increase the recovery of metals from the ash. Similarly, roasting in an oxygen enriched atmosphere does not affect the eventual metals recovery. Roasting in neutral or reducing atmospheres significantly reduces the recovery and will be discussed later.

In the static bed roasting used in this study, reducing the roasting time below 6 hr reduces the metal recovery. This reduction is due to the oxygen requirement for the

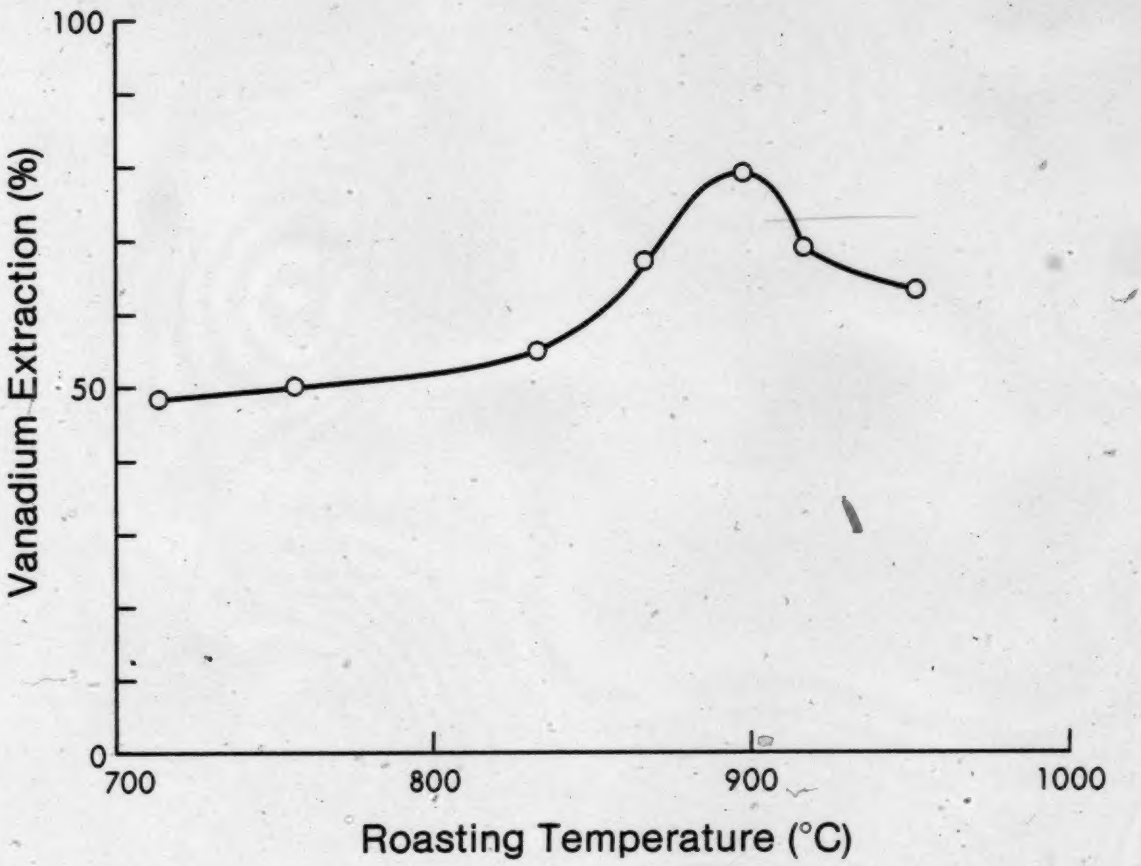


Figure 9. Dependence of vanadium extraction on roasting temperature with water leaching

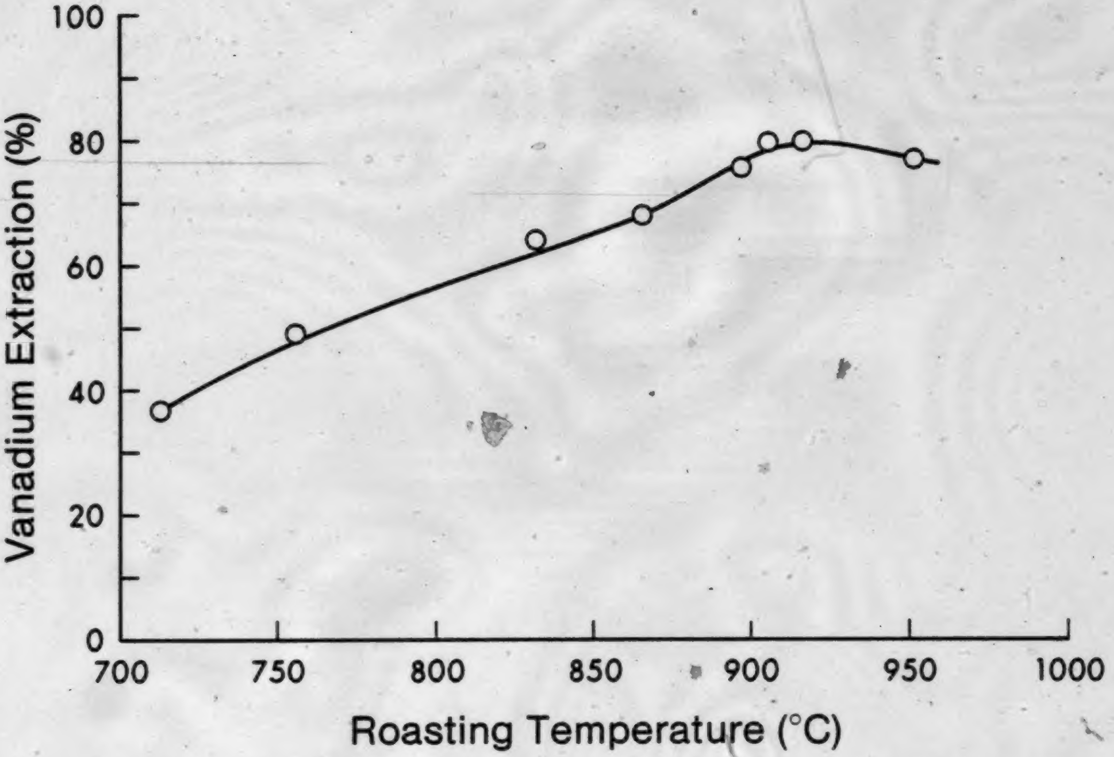


Figure 10. Dependence of vanadium extraction on roasting temperature with NaOH leaching

roasting reactions (see the next chapter) to occur. Thus, roasting for less than 6 hr is insufficient for the reactions to occur throughout the ash bed (depth = 2 cm). Obviously, this roasting time may be reduced by the use of a fluidized bed or a rotating kiln.

NaCl Additions

The quantity of sodium chloride added to the ash is important in maximizing extraction and economic efficiency. Previous tests have shown that with roasting at 800°C vanadium extraction is 68.8% with 20 wt % sodium chloride; and approximately 52 wt % with 10% sodium chloride.

Figure 11 shows the vanadium extraction results of water leaching of Suncor I ash roasted at 905°C with varying quantities of sodium chloride. Although the optimum quantity of sodium chloride used will be an economic decision, in all other tests 14 wt % sodium chloride was added.

Leaching Conditions

The four variables that are examined involving the leaching process are solution pH, leaching temperature, leaching time and phase ratio. The ash used for these tests was roasted at 905°C with 10 wt % sodium chloride.

The pH of the leachant was varied from 5.20 to 12.48 by the addition of sulphuric acid or sodium hydroxide solution. The vanadium extraction varied irregularly from 70 to 80% over this range; the best extraction was obtained with water

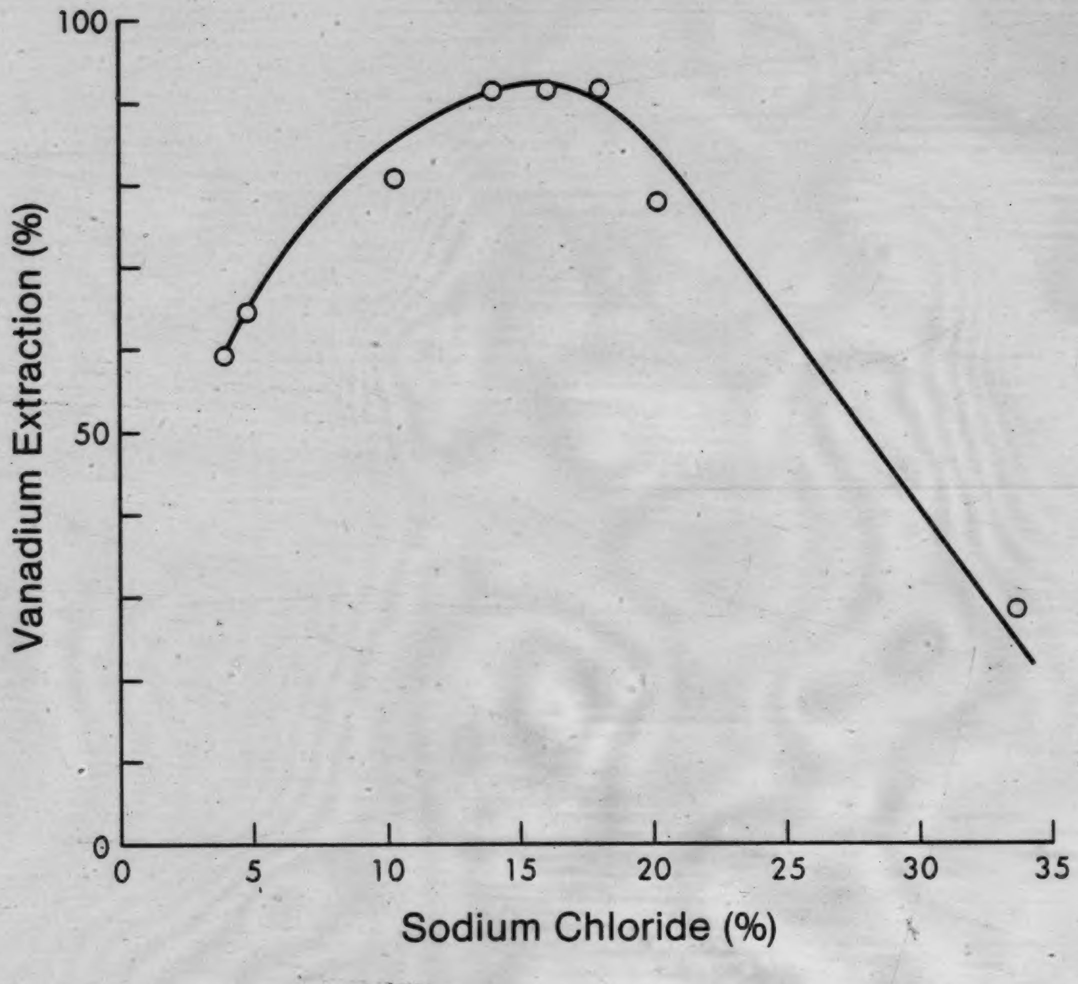


Figure 11. Dependence of vanadium extraction on NaCl additions

direct from the supply system with a pH of approximately six.

The effect of leaching temperature, with a 4 hr leach time, is presented in Fig. 12. The best vanadium extraction (81.1%) is obtained by leaching at the boiling point of the slurry. Additionally, Fig. 13 shows that the optimum extraction can be obtained after approximately 1 hr of leaching. Increasing the mixing efficiency by using a high temperature shaker bath does not increase the vanadium recovery.

Under the optimum conditions, roasting at 905°C with 14 wt % sodium chloride and leaching with water at 97°C for 1 hr the maximum vanadium extraction of approximately 90% is maintained up to a phase ratio of 1 g/ml. As the phase ratio increases to 5 g/ml, the vanadium extraction decreases to 74%.

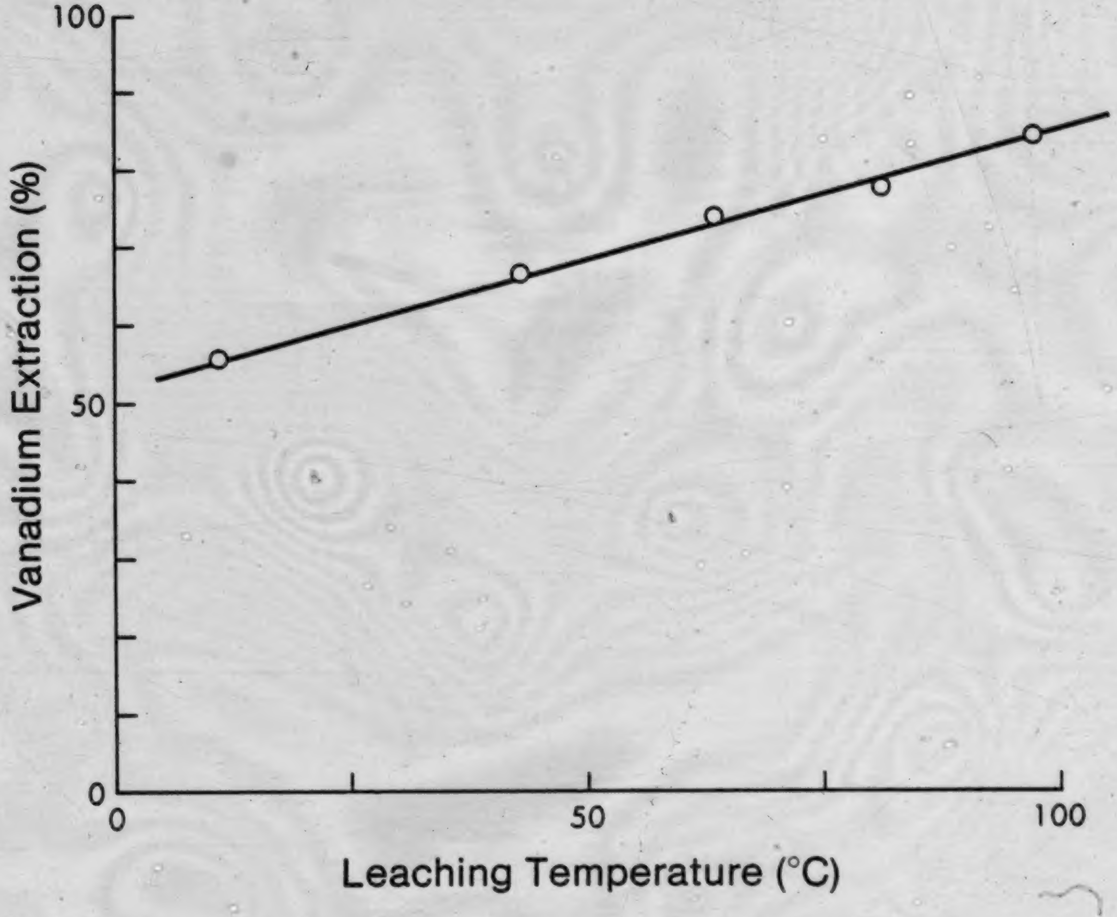


Figure 12. Dependence of vanadium extraction on leaching temperature

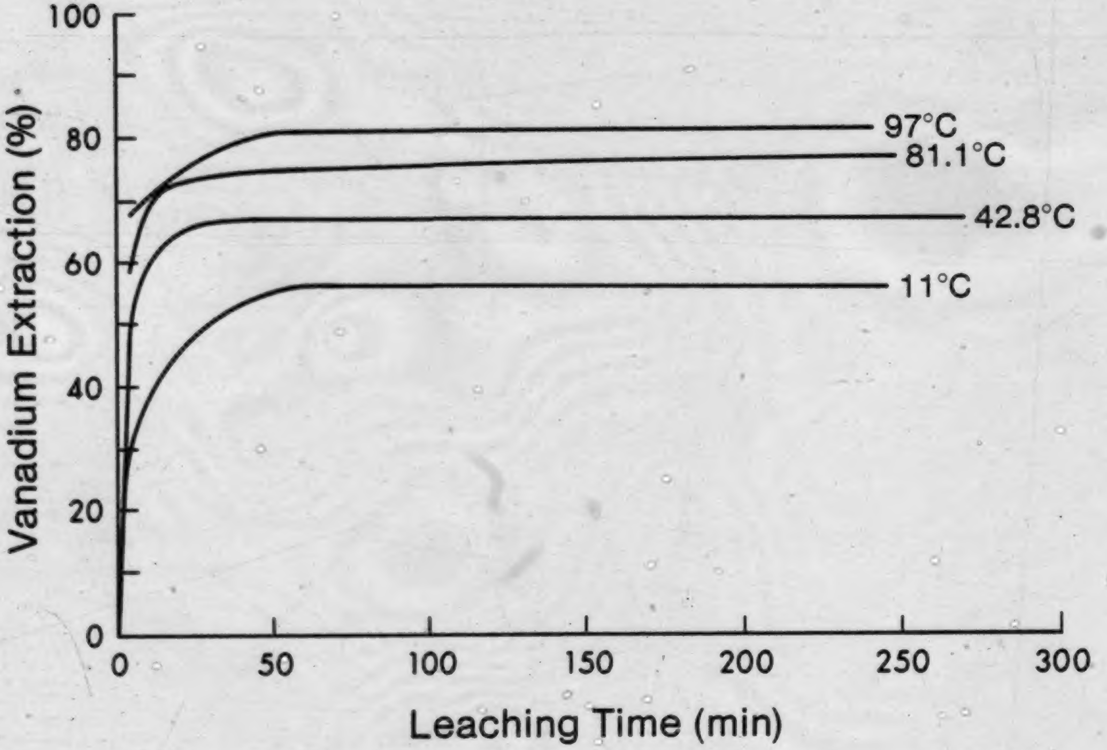


Figure 13. Dependence of vanadium extraction on leaching time at various temperatures

B. NICKEL

From the preliminary extraction studies, it appears that the highest nickel extraction from Suncor ash is obtained by roasting the ash with sulphur and subsequent leaching with sulphuric acid. This section of the study is aimed at optimizing the extraction conditions, mainly with regard to the following variables:

1. leaching medium
2. roasting temperature
3. sulphur additions
4. concentration of leachant
5. leaching conditions

The experimental conditions were similar to those used in the previous tests. Approximately 10 g of ash plus additive was roasted in a muffle furnace in air, with the temperature controlled to ±2°C. Leaching was carried out at 97°C for 4 hr, with a phase ratio of approximately 3 ml/g of roasted ash and mixing under reflux conditions. The hot slurries were filtered and the filtrate analyzed, after cooling, by atomic absorption spectroscopy.

Leachant

The preliminary results of the leaching of sulphur roasted ash with sulphuric acid produced a reasonable nickel dissolution. The extraction of nickel, vanadium and iron from ash roasted with 20 wt % sulphur by leaching with various reagents is shown in Table 20. Although all the

Leachant	Extraction Ni	 V	 Fe
H_2O	nd	24	nd
10% NaOH	nd	22.1	nd
10% H_2SO_4	93.5	46.9	18.5
10% HCl	72.4	45.3	17.7
10% HNO_3	52.1	46.5	9.6

nd: not detected

Table 20. Sulphur roast leachant extractions (%)

acids extract some quantity of the nickel and vanadium, the highest extraction is obtained with sulphuric acid which was used in all the future leaching studies.

Roasting Conditions

Prior to leaching with 10% sulphuric acid, the ash was roasted with 10 wt % sulphur at various temperatures for approximately 6 hr. The vanadium and nickel extractions are presented in Fig. 14.

The optimum extraction of nickel occurred after roasting at approximately 900°C. The highest vanadium and iron recoveries (34.8% and 17% respectively) were also obtained at this temperature. The iron recovery varied very little over the temperature range examined; from 14.3% at 200°C to 13.6% at 1050°C.

The variables that affect the roasting time are similar to those discussed previously. The effect of roasting in neutral, reducing and sulphur dioxide atmospheres will be discussed later.

Sulphur Additions

Figure 15 shows the nickel and vanadium extractions from the 10% sulphuric acid leaching of Suncor I ash roasted with variable quantities of sulphur at 900°C. The iron extraction, not included in Fig. 15, varied from 10.6% at 5 wt % sulphur to 20.2% at 25 wt % sulphur.

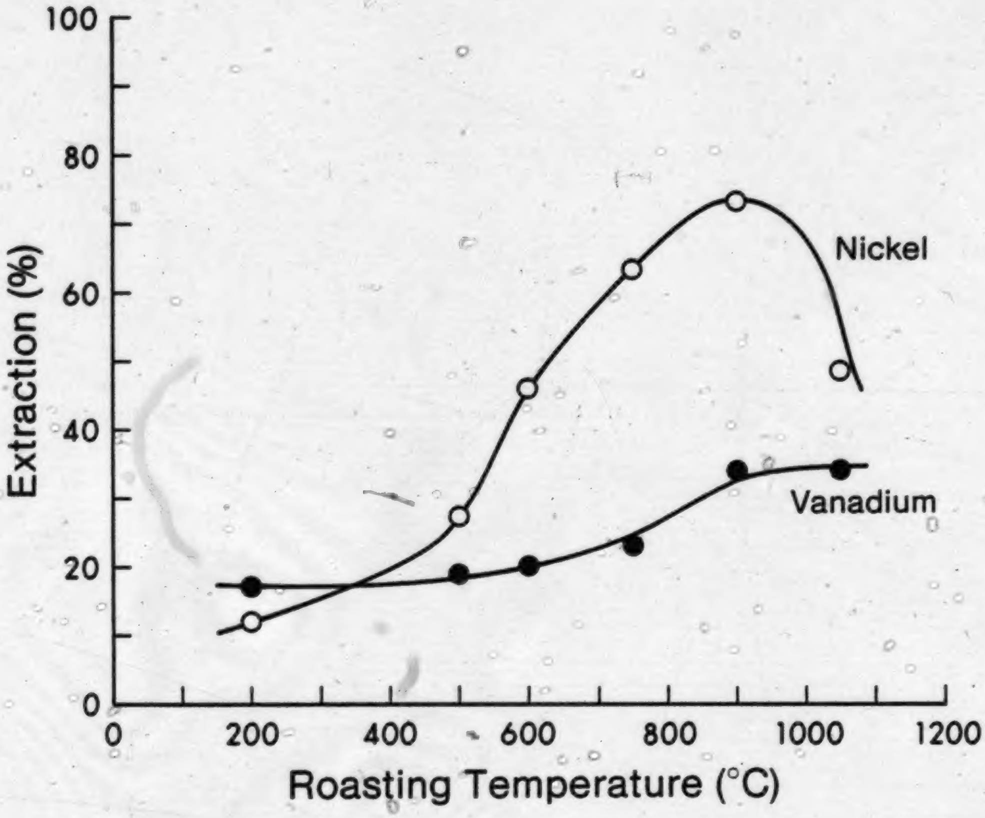


Figure 14. Dependence of vanadium and nickel extractions on roasting temperature

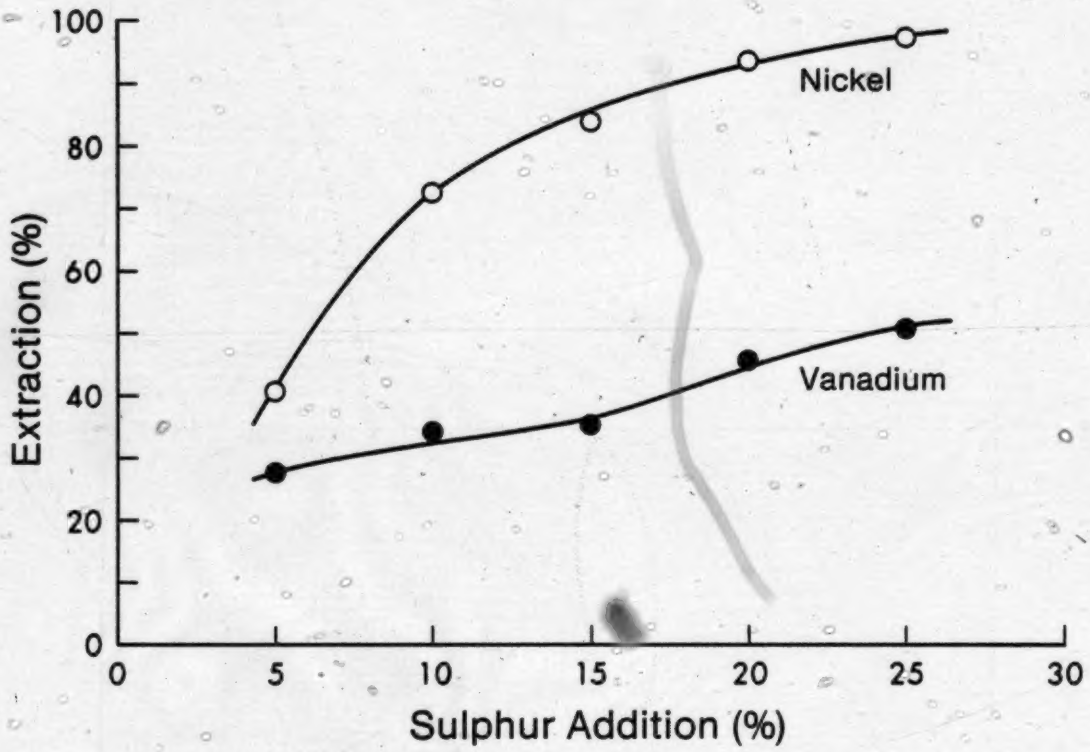


Figure 15. Dependence of vanadium and nickel extractions on sulphur additions

Although the optimum addition of sulphur must be made by an economic analysis of the overall extraction procedure, 20 wt % sulphur was added to the ash in all the following tests.

Leaching Conditions

The variables involved in the leaching process that are examined include concentration of the sulphuric acid leachant, leaching temperature and leaching time. The material used for these tests was Suncor I ash roasted at 900°C with 20 wt % sulphur.

Table 21 shows the nickel and vanadium recovery from the ash produced as above, with various sulphuric acid strengths. Although the highest extraction is obtained at a concentration of 15% sulphuric acid, the approximate optimum recovery can be considered to occur with approximately 10% sulphuric acid. The acid usage during leaching is very small; the acid molarity decreases from 1.1 to 1.0.

Figure 16 shows the effect of leaching temperature, with a four hour leach time, on nickel extraction, and Fig. 17 demonstrates the effect of leaching time at 98°C. Optimum leaching conditions may be estimated to require leaching for at least 1 hr at a temperature of approximately 98°C. Nickel extractions of 90% are maintained, with a leaching time of 2 hr at 98°C, up to a phase ratio of 1 ml/g.

Sulphuric acid (%)	Extraction V	 Ni	 Fe
5	42.0	50.0	11.6
10	46.9	93.5	18.9
15	49.7	96.7	20.2

Table 21. Effect of acid strength on sulphur roast extractions (%)

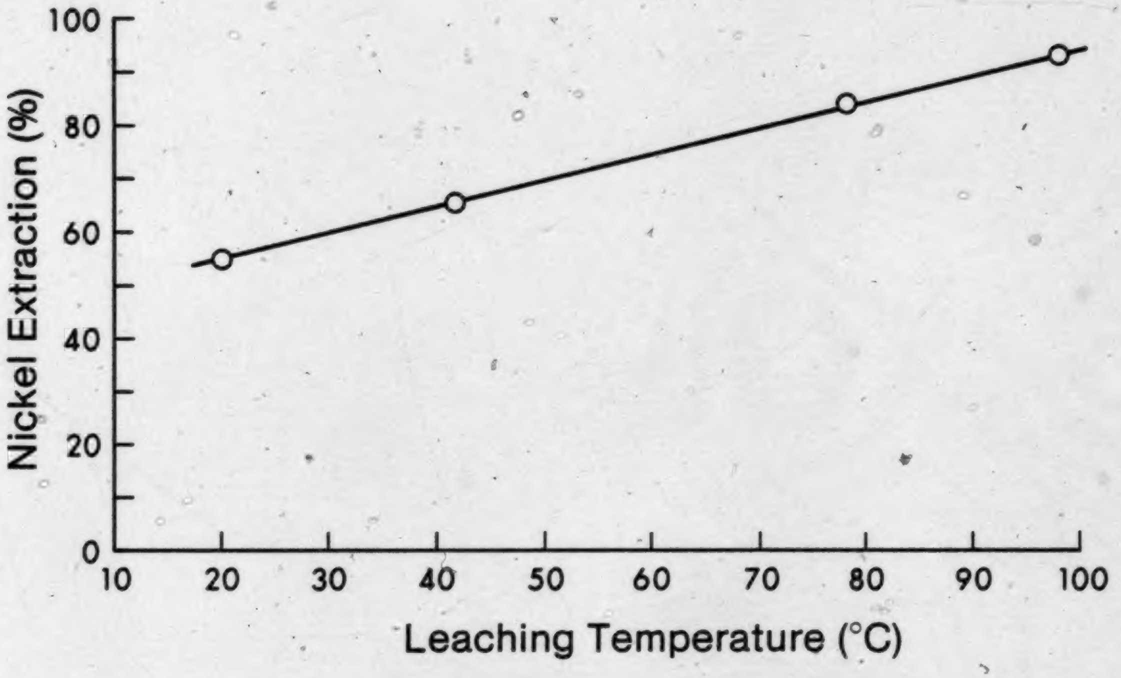


Figure 16. Dependence of nickel extraction on leaching temperature

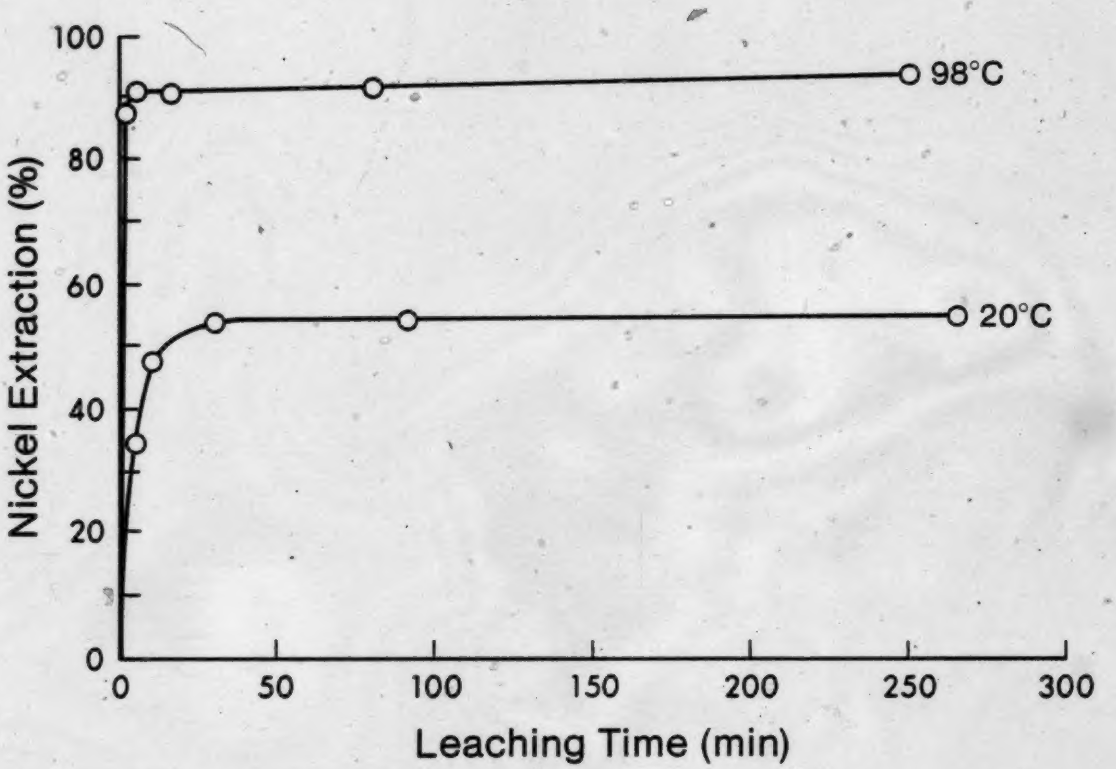


Figure 17. Dependence of nickel extraction on leaching time at temperatures of 20° and 98°C

C. EXTRACTION SUMMARY

For an industrial process the optimum extraction conditions must be evaluated with the aid of a detailed economic analysis of the process. However, in this thesis, the optimum conditions were estimated by attempting to balance recovery against reagent usage or time requirements.

The optimum conditions selected for the recovery of vanadium and nickel from the Suncor I ash were applied to the other Suncor ashes and the Syncrude ash samples. The leachates were analyzed by atomic absorption spectroscopy for several metals to determine the contaminants in the solution. These results are useful in comparing the extraction routes with other recovery processes for vanadium and nickel and suggesting further purification procedures.

Vanadium

The optimum vanadium extraction conditions determined from the previous tests are:

roasting temperature: 905°C
roasting atmosphere: air
roasting time: approx. 6 hr
roasting additive: 14 wt % sodium chloride
leaching solution: water
leaching temperture: 97°C
leaching time: approx. 2 hr
phase ratio: 1 ml/g of roasted ash

The four Suncor ashes and the two Syncrude ashes were treated under the optimum vanadium extraction conditions. After leaching, the hot slurries were filtered and washed by an equal volume of water. The leachates were then analyzed, by atomic absorption spectroscopy, for several elements.

For the Suncor ashes the extraction of vanadium was:

Suncor I	91.2%
Suncor II	89.3%
Suncor III	85.4%
Suncor IV	95.6%

The concentrations of the other major elements in solution are:

0.00 - 0.01 g/l: Ti, Ni, Cu, Zn
0.01 - 0.10 g/l: Fe, Al
0.10 - 1.00 g/l: Mn, Mo, Mg, Ca
1.00 - 3.00 g/l: K
>8 g/l: Na
10 g/l: V

For the two Syncrude ash samples the vanadium recoveries are approximately 7%. The nickel and iron recoveries are <0.01% and 0.02% respectively.

The factor limiting vanadium recovery from Syncrude ash is the high carbon content. If the ash is initially roasted in air to remove the carbon, then roasted with 10 wt % sodium chloride, the vanadium recovery is approximately 75%. The nickel and iron recoveries both remain <1%.

Nickel

The optimum nickel extraction conditions determined from the previous tests are:

roasting atmosphere: air
roasting temperature: 900°C
roasting time: approx. 6 hr
roasting additive: 15 wt % sulphur
leaching solution: 10% sulphuric acid
leaching temperature: 98°C
leaching time: approx. 2 hr
phase ratio: 1 ml/g of roasted ash

The four Suncor ashes were treated under the optimum nickel extraction conditions. After leaching, the hot slurries were filtered and washed with an equal volume of water. The leachates were then analyzed by atomic absorption spectroscopy. The nickel extraction from the Suncor ashes was:

Suncor I	93.2%
Suncor II	97.6%
Suncor III	94.1%
Suncor IV	82.3%

The produced solution contained approximatelt 3.3 g/l nickel. The concentration of the other major elements in solution are:

0.0 - 0.1 g/l: Cu, Zn, Ca, Mn
0.1 - 1.0 g/l: Mo, K, Mg
1.0 - 5.0 g/l: Fe, V, Ti, Na
>10 g/l: Al

For the two Syncrude ash samples the nickel recoveries in solution are approximately 55%. The vanadium and iron recoveries are 40.7% and 39.9% respectively. Nickel recovery was not increased by pre-roasting the ash in air to remove carbon. Additionally, sulphur is not responsible for the metal extractions from Syncrude ash. Similar nickel, vanadium and iron extractions can be obtained by treating Syncrude ash roasted at 600°C with 20% sulphuric acid. It is probable that the nickel may not be present in the Syncrude ash in a similar form to the Suncor ash, since they are formed under different conditions.

Only vanadium can be extracted to any extent by water or acid from Suncor I ash roasted with a mixture of sodium chloride and sulphur at 900°C.

V. DISCUSSION

A. VANADIUM EXTRACTION

Further Processing

The processing of vanadium ores by sodium salt roasting and water leaching generally produces a solution containing 7-20 g/l vanadium. To produce a high grade vanadium pentoxide product or to upgrade an impure vanadium solution, the vanadium can be extracted from an acidified solution by solvent extraction. The vanadium is then recovered from the purified solution as ammonium metavanadate by precipitation with an ammonium salt.

An alternative procedure, more commonly used, is to acidify the solution to a pH of 2.4-2.8, then precipitate the vanadium with ammonium chloride. The final ammonium metavanadate product is roasted to form vanadium pentoxide, which is a commercial product in any grade in excess of 83%. Impure vanadium pentoxide may be purified by digestion in sodium carbonate solution and precipitation with ammonium chloride or sulphate.[53]

Table 22 shows the concentration of various elements in a typical Suncor ash leachate and the composition of the final oxide product. The leachate was acidified from a pH of 7 to 2.5, then the stoichiometric quantity of ammonium chloride was added, according to the reaction,

Element	Leachante (g/l)	Oxide product (%)
V	13.0	73.4
Fe	0.01	0.05
Mn	0.09	0.63
Ni	0.008	0.03
Zn	0.01	0.05
Mo	0.36	1.25
Al	0.06	0.49
K	1.74	9.84
Mg	0.30	2.15
Ca	0.98	6.13
Na	10	6

Table 22: Solution and oxide product composition

$$VO_3^- + NH_4^+ \longrightarrow NH_4VO_3$$

The stoichiometric quantity of ammonium chloride precipitates 70% of the vanadium to produce, via the reaction,

$$2NH_4VO_3 \longrightarrow V_2O_5 + H_2O + 2NH_3$$

a solid containing 73% V_2O_5. The oxide product can be increased to 88% V_2O_5 by increasing the recovery from solution to 81% with twice the stoichiometric quantity of ammonium chloride.

A detailed economic study is required to evaluate the use of Suncor ash as a source of vanadium. However, similar processes are currently producing vanadium economically in the United States. Thus the process may be feasible if sufficient markets can be located.

Roasting Reactions

The first detailed study of the salt roast-water leach process for vanadium recovery was carried out by Dresher.[154] The basic roasting reaction can be written as

$$V_2O_5 + 1/2O_2 + 2NaCl \longrightarrow 2NaVO_3 + Cl_2$$

$$V_2O_3 + 3/2O_2 + 2NaCl \longrightarrow 2NaVO_3 + Cl_2$$

and his conclusions can be summarized as:

a. The initial portion of the roasting reaction rate curve follows the parabolic rate law, indicating diffusion of either oxygen or chlorine through the reaction products.

b. After the initial period, the reaction rate curve follows the logarithmic rate law. This is interpreted as hindered diffusion of the gas

> "by the presence of barriers consisting of small blisters or pockets which interrupt the straight-line diffusion of the gas through the accumulated reaction products."

c. Oxygen partial pressure does not affect the roasting reaction rate.

d. There is a significant reaction rate increase at the melting point of sodium chloride.

e. The main rate controlling step for the formation of sodium metavanadate is the diffusion to the reaction site of oxygen or the diffusion of chlorine from the reaction site.

Salt roasting of Suncor ash produced some results that were in agreement with Dresher's study. Although the final sodium vanadate compound was not identified, its formation requires oxygen, as roasting in neutral and reducing atmospheres (N_2 and H_2) led to vanadium extractions of 0.6% and 1.0%, respectively. The only other conclusion of this type to be made is that carbon is not required for the formation of the water soluble vanadium compound. Initial ash roasting at 650°C followed by salt roasting led to 86.5% vanadium recovery compared to 89.1% by direct salt roasting.

Although the roasting reaction rate was not measured, it was observed that increasing the oxygen partial pressure did not affect the vanadium recovery. Additionally, there was a noticeable increase in vanadium recovery at roasting temperatures above the melting point of sodium chloride (801°C), but no observations of the reaction rate were made. Dresher also noted that the optimum concentration of sodium chloride is 6% plus 1% per % V_2O_5. The optimum requirement for Suncor ash is slightly above this value.

A study of the salt roasting of vanadium-rich titaniferous magnetites[155] showed an appreciable increase in vanadium extraction above the melting point of sodium chloride and a maximum vanadium extraction after roasting at 850°C. The maximum extraction was obtained with a $NaCl/V_2O_5$ ratio of approximately 5.

However, a similar study[156] found that the maximum extraction occurred after roasting at 950°C with 12% NaCl from an ore containing 0.9% V_2O_5. Five times the stoichiometric quantity of ammonium chloride was required to precipitate 98% of the vanadium. The results from these studies compare reasonably with the optimum conditions for the Suncor ash vanadium extraction.

The replacement of sodium chloride by another sodium salt has also been examined.[157] Sodium chloride is reported as being selective for vanadium whereas sodium carbonate will form water soluble compounds with silica, phosphorus and alumina. Sodium sulphate requires a higher roasting temperature and is normally more expensive.

A vanadium recovery of 89.1% from Suncor ash was increased to 93.5% by using an additive of 5% Na_2CO_3/5% NaCl and decreased to 68.4% by using 14% KCl as the additive. However, sodium carbonate will increase the contaminants in solution and decrease the purity of the final product. Roasting with a calcium compound produces a water insoluble calcium vanadate.

The vanadium recovery from Suncor ash was not altered by grinding the ash to 90% less than 20 μm in diameter. The finer particles should make available more surface area and hence more vanadium to chemical reaction. The absence of an extraction increase may have two explanations.

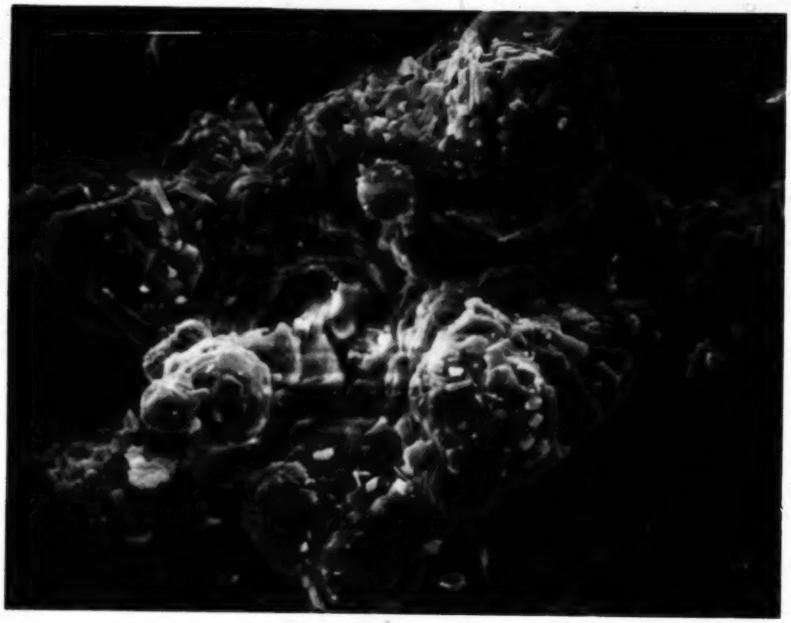
The vanadium may occur in the ash in different compounds, not all of which react with sodium chloride to form a water soluble vanadium compound. Therefore increasing the surface area may not increase the vanadium extraction. The extraction increase with the roasting addition of sodium chloride and sodium carbonate may suggest that some vanadium compounds will react in the required manner with sodium carbonate but not with sodium chloride.

Alternatively, the vanadium may react with some of the calcium in the ash to form a water insoluble calcium vanadate. Formation of a calcium/vanadium compound has previously occurred during sodium carbonate roasting of vanadium rich slags.[158]

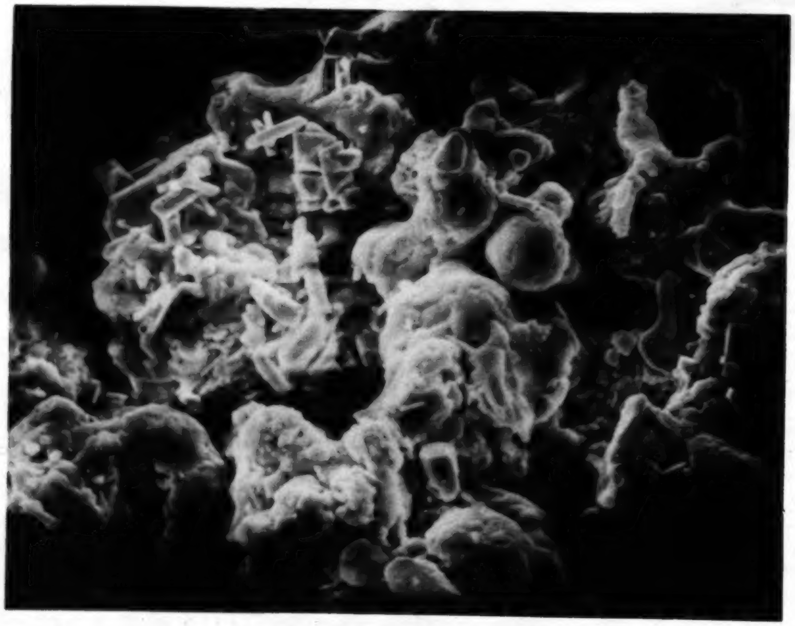
X-Ray/SEM Studies

X-ray diffraction scans of various roasted ashes and residues produced few identifiable compounds using the ASTM Powder Data File. The only firm identification is for the silicate 1-x $NaAlSi_3O_{16}$, x $CaAl_2Si_2O_{16}$ in the residues. Additionally, sodium chloride is found in the roasted ash prior to leaching. The three major x-ray diffraction scan peaks of an iron vanadium oxide, $Fe_{2.6}V^{+5}_{1.5}V^{+3}_{5.5}O_{16}$, were found in the residue scans. The lack of confirming peaks and the small quantity of vanadium in the residue suggest that this compound may not be present. Chursina and Gutermakher[159] suggest that reacting ash with hydrofluoric acid on a water bath will dissolve silica and some silicates, which will enhance the residual x-ray diffraction patterns. Ash, carbon free ash, roasted ash and residue were treated by this technique but no change in the diffraction patterns was observed.

Suncor ash before treatment is shown in Photograph 1, its appearance after roasting with 14 wt % sodium chloride at 905°C is shown in Photograph 5. The elemental EDA scans of the sample indicate that the surface material is rich in sodium, vanadium, iron and titanium. After leaching, Photograph 6, much of the surface material has been removed. The structure of the residue appears to be divided into three types: (1) apparently untouched ash spheres of similar composition to the original material, (2) surface growths rich in titanium and iron, and (3) ash spheres (rich in iron



Photograph 5: Suncor ash after roasting with NaCl (100 μm)

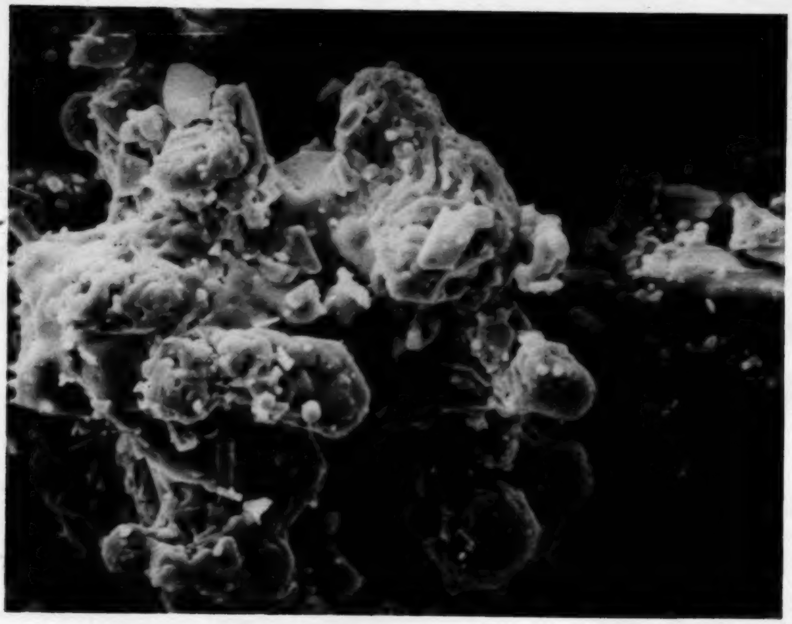


Photograph 6: Suncor ash after water leaching (100 μm)

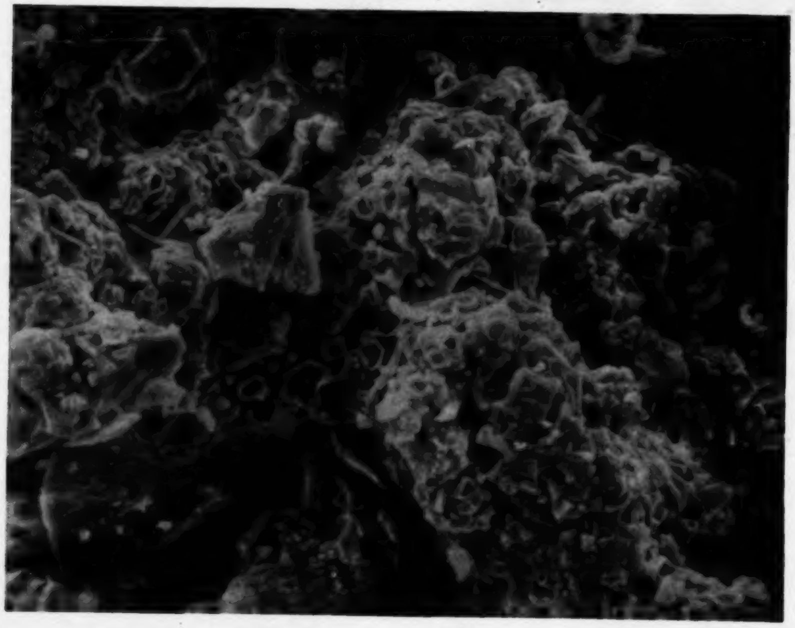
and silicon) that have been partially destroyed to reveal a hollow interior. The presence of untouched ash spheres indicates that some of the vanadium has not reacted with the sodium chloride.

Photographs 7 and 8 show the ash after roasting with 33.6 wt % sodium chloride at 905°C and the ash after roasting with 14 wt % sodium chloride at 1050°C. In Photograph 7, after roasting with excess sodium chloride, the ash appears to have a smoother surface finish which normally indicates melting has occurred. The decrease in vanadium extraction with excess sodium chloride may have two possible explanations:

1. When sodium chloride melts at 801°C the solid-solid-gas reaction is converted to a more favorable solid-liquid-gas reaction. The salt-ash contact is increased but the oxygen-ash contact is decreased as the molten salt becomes a barrier between the two phases. One study[55] suggests that this molten salt barrier is the reason for little improvement in vanadium recovery above 850°C. However, no examination is made of the effect of increasing the temperature above 900°C or increasing the sodium chloride content. If the molten salt does act as a significant barrier to oxygen reaction with the ash, one would expect large quantities of sodium chloride to increase the barrier to an extent where vanadium recovery would decrease.



Photograph 7: Suncor ash after roasting with 33.6 wt % NaCl (100 μm)



Photograph 8: Suncor ash after roasting at 1050°C (100 μm)

2. The alternative explanation of the extraction decrease is that the increase in sodium chloride content decreases the melting point of the ash mixture and forms a molten sodium silicate. Thus, on cooling a vanadium oxide or sodium vanadate is physically trapped within the silicate.

Roasting the ash with 14 wt % sodium chloride at 1050°C also leads to a decrease in vanadium recovery, although Photograph 8 shows no substantial differences from those of ash roasted at 905°C. Silitonga and Prosser[158] found vanadium to be present in a slag as $FeO(V,Fe)_2O_3$ which reacted with sodium carbonate to form sodium vanadate. However, at temperatures above 1000°C the sodium vanadate reacted with the silicate to physically trap the vanadium in a sodium vanado-silicate glass. A similar mechanism could account for the decrease in vanadium extraction after roasting at high temperatures.

The x-ray and SEM studies, and reports from other investigators, suggest that the vanadium exists in the ash as an oxide, probably as a mixed oxide with iron.

B. NICKEL EXTRACTION

Further Processing

Treatment schemes for nickel containing acid solutions generally fall into two groups; electrowinning and sulphide precipitation. The electrowinning of nickel from solution requires a pure (low Cu, Fe, Co), high nickel concentration (60 g/l) solution. The sulphide precipitation route is used for low concentration solutions (6 g/l) that are generally produced by sulphuric acid pressure leaching of oxidized nickel ores. A typical solution (5 g/l Ni, 0.8 g/l Fe, pH 2) would be reacted with hydrogen sulphide to precipitate a high grade nickel sulphide. To obtain metallic nickel, the sulphide is redissolved, impurities precipitated and 99% nickel metal recovered by electrowinning.

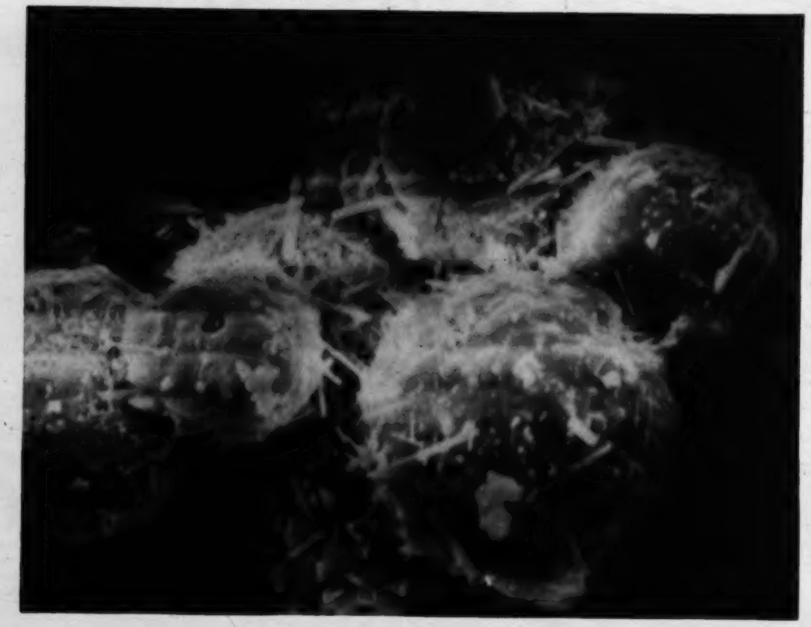
The solution produced from the leaching of Suncor ash contains adequate nickel, but the acidity of the solution must be reduced. The high iron concentration would result in the formation of iron sulphide; this formation can be prevented by initial aeration of the solution which will precipitate iron(III) hydroxide. The effect of the high concentrations of sodium, vanadium and titanium on the sulphide precipitation is unknown.

X-Ray/SEM Studies

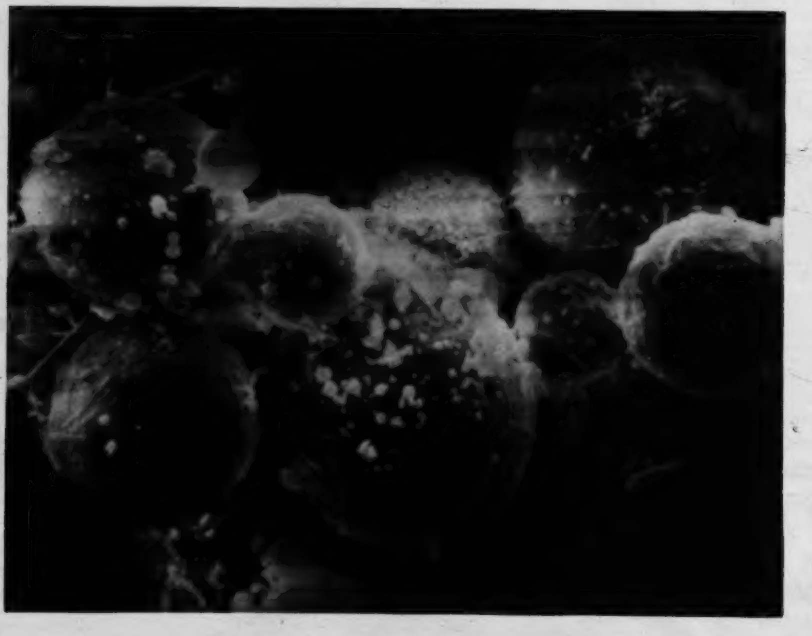
X-ray diffraction analysis of the various sulphur roasted ashes and residues produced very few diffraction scan peaks and no identifiable compounds could be located in the ASTM Powder Diffraction Data File. Similar results were obtained for ash roasted with pyrite, sulphur dioxide, pyrrhotite and sodium sulphate with the exception of identifying unreacted pyrite and pyrrhotite. (The extractions from these roasted ashes will be discussed later.)

Suncor I ash before treatment is shown in Photograph 1; its appearance after roasting with 10 wt % sulphur at 900°C is shown in Photograph 9. The crystals that have formed on the surface of the spheres appear rich in vanadium, nickel, iron and titanium, or some combination of these elements. The sulphur content of the roasted ash was 0.34%, virtually identical to that of pure ash roasted at 900°C (0.35%), indicating that the residual sulphur is present due to the sulphur in the original ash. The crystals appear similar to the microcrystals originally present in the ash (Photograph 3) and, since they contain very little or no sulphur, they are probably oxides.

Photograph 10 shows the ash after leaching with 10% sulphuric acid. The majority of the crystals have been removed from the surface of the spheres during the leaching process. Additionally, the sulphur content of the ash has been reduced to 0.01% so that the acid has leached the oxide



Photograph 9: Suncor ash after roasting with sulphur (10 μm)



Photograph 10: Suncor ash after sulphuric acid leaching (10 μm)

crystals and the inorganically bound sulphur.

As is shown in Photograph 11, increasing the initial sulphur addition to 50 wt % significantly increases the formation of microcrystals. The nickel extraction is also increased from 72.8% to greater than 97%.

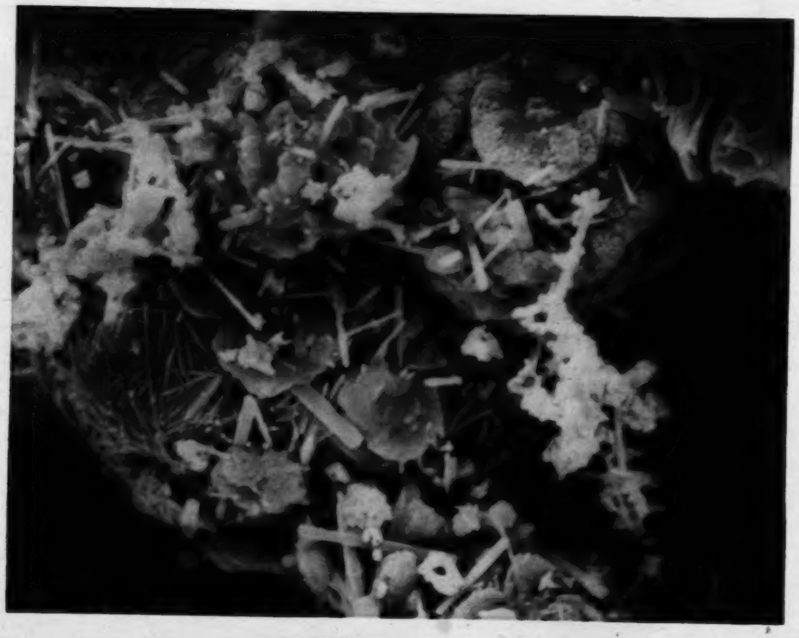
The effect of roasting the ash with sulphur in neutral or reducing atmospheres was also investigated. Photograph 12 shows the ash after roasting with 10 wt % sulphur at 900°C in argon. The surface growths on the spheres appear to be rich in vanadium, iron, nickel and possibly aluminium. The growths were also rich in sulphur; the ash contained >2% sulphur.

Roasting the ash and 10 wt % sulphur at 900°C in a flowing hydrogen stream produced apparently unaltered ash that contained 0.5% sulphur. The nickel extraction from the ash roasted in neutral and reducing conditions was 12.7% and 3.2% respectively.

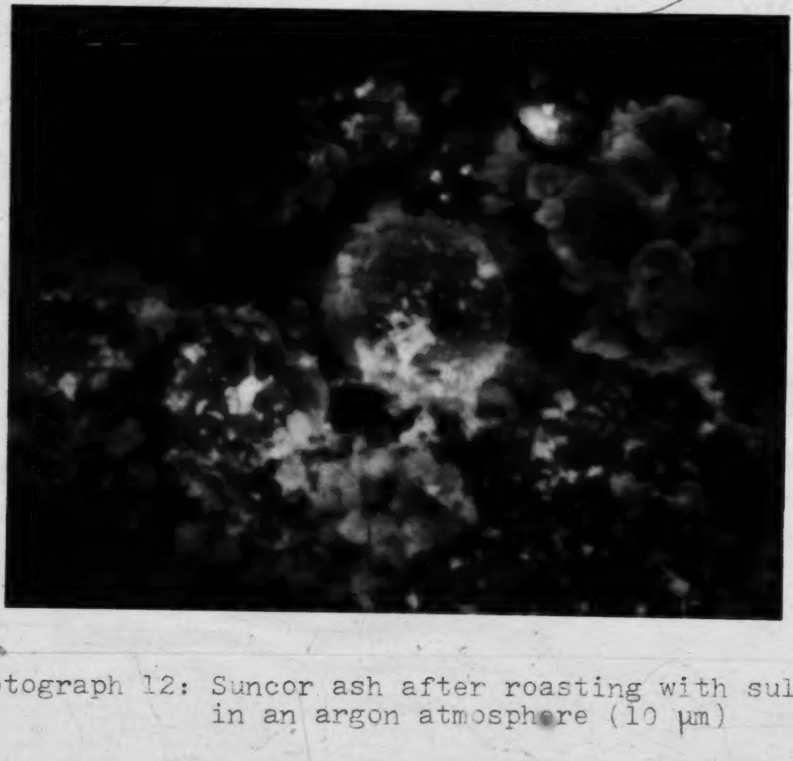
The results to this stage can be summarized as:

1. During roasting in air the sulphur may vaporize and dissipate, it may react with oxygen to form sulphur dioxide or it may react with the ash. Microcrystals that probably contain an acid soluble nickel oxide are formed.

2. During roasting in argon the sulphur may vaporize and be carried off in the gas stream or it may combine with the ash. Surface growths formed on the ash spheres probably contain a slightly acid soluble nickel sulphide.



Photograph 11: Suncor ash after roasting with 50 wt % sulphur (10 μm)



Photograph 12: Suncor ash after roasting with sulphur in an argon atmosphere (10 μm)

3. During roasting in hydrogen, the sulphur may vaporize and be carried off in the gas stream, it may react with the ash or it may form hydrogen sulphide.

The decrease in nickel extraction at roasting temperatures below 900°C is shown in Fig. 14. The residual sulphur content of these ashes and their appearance was:

900°C	0.34%	microcrystals
750°C	0.60%	microcrystals
650°C	0.84%	small crystals
500°C	>2%	surface growths
200°C	>2%	no growths

From these reactions and the EDA analyses of the ash growths and crystals it appears that at 500°C in air or in a neutral atmosphere, the nickel in the ash reacts to form nickel sulphide. At 650°C in air, the nickel sulphide reacts with oxygen to form nickel oxide.

Roasting Reactions

Free energies of various reactions at standard conditions can be evaluated from the available data[168] to discuss the possible reactions from a thermodynamic viewpoint. However, no analysis can be made of the kinetics of any of the reactions that are thermodynamically feasible.

Thermodynamically, sulphur will react with hydrogen and oxygen at 200°C. The reaction free energies increase as the temperature increases so that the thermodynamic driving force for the reaction will decrease. However, the reactivity of the sulphur will increase as it melts (120°C) and vaporizes (445°C). Thus it is impossible to easily evaluate the extent to which these reactions occur under the roasting conditions. Although, it is apparent that the sulphur will react with hydrogen before the ash, and with the ash before oxygen.

The other reaction suggested by the SEM studies was the reaction between nickel sulphide and oxygen at approximately 650°C. Thermodynamically, this reaction is feasible:

$$NiS + 3/2O_2 \longrightarrow NiO + SO_2 \quad \Delta G = -88 \text{ kcal}$$

The other requirement of the suggested reaction scheme is that the nickel originally present in the ash will react at 500°C with sulphur, to form nickel sulphide.

The simplest nickel compounds that could be suggested to occur in the ash are:

nickel oxide, NiO
nickel sulphide, NiS
nickel sulphate, $NiSO_4$
nickel silicate, $NiSiO_3$
nickel laterite, $(Mg,Ni)SiO_3$

If the initial nickel compound is nickel sulphide, it would be expected that roasting the ash at >650°C in air and leaching with acid would extract the nickel into solution. But the recoveries after roasting in air or argon at 800°C followed by sulphuric acid leaching were only 2.3% and 0.1%, respectively.

If the initial compound was nickel sulphate, the nickel should be directly water soluble; similarly, nickel oxide should be directly acid soluble. However, the nickel dissolution for these leaching conditions was 2.3% and 11.8% respectively.

Nickel silicate could be considered a type of nickel laterite which is of the general form $(Ni,Mg,Fe)SiO_3$ with a variable composition. The treatment of laterites of varying composition is carried out by several different schemes but some of them are similar to the process suggested for nickel recovery from Suncor ash.

The sulphidation of nickel ores was first reported by Filin et al.,[141] who used a mixture of sodium sulphate and wood charcoal roasted with the ore at 700°-950°C. The sulphidizing agent is reported to be sodium sulphide and the degree of sulphidation to be a linear function of temperature.

More recently, the sulphidation of nickel laterites has been examined by the Colorado School of Mines Research Foundation.[142] Approximately 15% sulphur is added to a slurry of laterite ore containing 2% nickel. The sulphur can be replaced by pyrite. The sulphidation reaction occurs at 230°-240°C with a pressure of 380-480 psig. The nickel sulphide is oxidized to nickel sulphate at a temperature of 200°C and a pressure of 210 psig. The nickel dissolves in a slurry at a pH of 1-2, extracting 85-95% of the nickel.

A recent patent[143] has stated that nickel can be recovered from laterites by roasting with sulphur followed by acid leaching, but no comments on the mechanism are made. The sulphur is reported to prevent the formation of insoluble forsterite, $2MgO.SiO_2$, during roasting.

Alternative nickel recovery schemes for laterites have involved reduction roasting/ammonia leaching,[144] [145] sulphuric acid pressure leaching[145] [146] and reduction roasting with pyrite to form nickel sulphate.[147]

The similarity between the sulphidation studies and the Suncor ash treatment scheme, associated with the good nickel recovery by sulphuric acid pressure leaching (a typical laterite treatment route), indicates that the nickel is present in the ash as a laterite. Roasting the ash with sulphur produces nickel sulphide which is subsequently oxidized to an acid soluble nickel oxide.

Sulphur was replaced in the reaction by various other sulphur-containing additives. The roasted ash appearance after roasting at 900°C and the nickel extractions after 10% sulphuric acid leaching were:

sulphur	40.7%	microcrystals
pyrrhotite	4.2%	unaltered ash
pyrite	36.3%	microcrystals
sulphur dioxide	1.4%	unaltered ash
sodium sulphate	37.8%	microcrystals

The quantity of solid additive mixed with the ash was sufficient to produce a mixture containing 5 wt % sulphur.

The results indicate that if sulphur is available in a pure form, from the decomposition of pyrite,

$$2FeS_2 \longrightarrow 2FeS + S_2 \quad (900°C) \quad \Delta G = 19 \text{ kcal}$$

or from sodium sulphate, a slightly acid soluble nickel sulphide will be formed. Sulphur will not be available from the decomposition of pyrrhotite or sulphur dioxide as their free energies of formation are <-40,000 cal at 900°C.

C. ASH STRUCTURE

At various stages throughout this study comments on the structure of the Suncor ash have been made. These brief comments can be summarized as:

1. Previous studies have located irregular carbon grains and aluminosilicate spheres,[139] and coke particles, fly ash spheres, cenospheres, pleurospheres and enriched microcrystals[144] in the ash.

2. The esr spectrum of Suncor ash indicated the presence of magnetite and the existence of vanadium in the +3 and/or +5 oxidation states.

3. The vanadium and nickel distributions in the ash do not agree with the vaporization-condensation model.

4. SEM studies located distinct carbon grains, aluminosilicate fly ash spheres and cenospheres, and microcrystals enriched in iron, vanadium, titanium and nickel, and deficient in aluminium, silicon, calcium and potassium.

5. The vanadium recovery process suggests that the vanadium is present in the ash as a vanadium oxide. A mixed sodium-calcium-aluminium silicate and an iron vanadium oxide may also be present during the treatment process.

6. The nickel treatment scheme and the reports of other investigators indicate that the nickel may be present in the ash as a nickel laterite.

These results can be combined to suggest that components of the Suncor ash include distinct unburnt coke grains, magnetite, aluminosilcate spheres which may contain a vanadium oxide and a nickel laterite, and crystal growths on the sphere surfaces. The Syncrude ash has a high carbon content and is aptly described as unburnt coke.

VI. CONCLUSION

This thesis has succeeded in describing extraction processes for the recovery of vanadium and nickel from the Athabasca oil sands fly ash. It has also produced some evidence of the compounds and structure in the ash.

Approximately 90% of the vanadium can be extracted from Suncor ash by roasting the ash with sodium chloride and leaching with hot water. The produced solution is suitable for the production of commercial grade vanadium pentoxide. A similar procedure can be used with Syncrude ash if it is pre-roasted to lower the carbon content. Similar vanadium extraction processes are in commercial operation, so that it is probable if sufficient ash supplies and markets are available, that an industrial operation could be possible.

Approximately 90% of the nickel can be extracted from Suncor ash by roasting the ash with sulphur and leaching with sulphuric acid. Three major problems may prevent this process from economic consideration. The factors are:- 1) the small quantity of nickel in the ash compared to market requirements, 2) the inability to treat other ashes (e.g.,Syncrude), and 3) the high sulphur dioxide emissions from roasting with sulphur.

The Suncor ash was shown to contain some metal-rich crystals on the surfaces of the aluminosilicate spheres and may also have some enrichment of certain elements on the sphere surfaces. Additionally, the nickel extraction procedure indicates that the nickel is present in the ash as a laterite.

Further work should examine other ashes produced in the region as other plants start operation. An attempt can then be made to optimize, scientifically and economically, a process for recovering, at least vanadium, from all ashes of the Athabasca oil sands area.

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APPENDIX I

Figures 9 and 10

Temperature (^{o}C)	Vanadium Extraction (%)	
	Water	NaOH
713	48.5	36.4
756	50.1	48.8
832	54.8	63.9
866	67.1	68.1
897	79.2	76.1
905	81.5	79.1
917	69.2	79.7
952	63.3	77.3

Figure 11

NaCl (%)	Vanadium Extraction (%)
0	11.2
3.9	59.3
4.8	64.7
10.3	80.8
14.0	91.2
18.0	91.5
20.2	61.3
33.6	28.4

Figures 12 and 13

Temperature (^oC)	Time (min)	V Extraction (%)
11	2	9.7
	7	32.4
	20	45.0
	37	52.2
	240	55.6
42.8	2	30.2
	7	53.2
	20	65.0
	85	66.7
	270	67.1
63.3	240	73.9
81.1	5	63.4
	20	73.9
	66	73.9
	247	77.7
97	5	68.2
	20	73.9
	50	81.1
	263	81.1

Figure 14

Temperature (^oC)	V Extraction (%)	Ni Extraction (%)
200	17.1	12.2
500	18.9	27.4
600	20.1	46.2
750	23.0	62.9
900	34.2	72.8
1050	33.2	47.8

Figure 15

S Addition (%)	V Extraction (%)	Ni Extraction(%)
5	27.4	40.7
10	34.2	72.8
15	34.7	84.2
20	46.9	93.5
25	51.3	96.7

Figure 16

Temperature (°C)	Nickel Extraction (%)
20	55.0
42	65.8
78	83.6
98	93.5

Figure 17

Time (min)	Nickel Extraction (%)
3 (20°C)	34.3
10	47.1
30	54.0
90	54.5
265	55.0
1 (98°C)	86.6
5	92.0
15	91.8
80	92.1
250	93.5